UNIVERSITY OF MICHIGAN NOV 1957
PHYSICS LIBRARY

REGISTERED No. M. 3121

PROCEEDINGS

OF THE

INDIAN ACADEMY OF SCIENCES

VOL. XLVI] *SECTION A* [No. 3

SEPTEMBER 1957

Price Rs. 2 or 3 Sh. *Annual Subscription Rs. 18*

PRINTED AT THE BANGALORE PRESS, BANGALORE CITY, BY C. VASUDEVA RAO, SUPERINTENDENT, AND PUBLISHED BY THE INDIAN ACADEMY OF SCIENCES, BANGALORE

THE RAMAN SPECTRUM OF CALCITE AND ITS INTERPRETATION

By D. Krishnamurti

(*Memoir No.* 100 *from the Raman Research Institute, Bangalore-6*)

Received July 26, 1957

(Communicated by Sir C. V. Raman)

1. Introduction

The present memoir embodies the results of experimental studies undertaken in the newly built spectroscopic laboratory of the Raman Research Institute. It is also the first report on the results of a programme of research on the Raman spectra of crystals undertaken with a view to obtain a fuller experimental knowledge as well as a deeper theoretical understanding of the phenomena which present themselves in this field. The present memoir concerns itself with the case of calcite. This was, quite naturally, one of the crystals to be investigated by the earliest workers in the field. An extensive literature has therefore accumulated which deals with the Raman spectrum of calcite and its theoretical interpretation. Nevertheless, the present investigation has brought to light several new facts with important theoretical implications.

It appears appropriate in the present memoir to begin with a brief description of the special features of the new laboratory which was designed and built with a view to carrying out investigations in this field of research. It also appears appropriate to give some details of the experimental techniques adopted in the present investigation which have enabled the results described in it to be achieved.

2. The New Spectroscopic Laboratory

The Raman effect being inherently a phenomenon of low intensity, its study usually requires the employment of fast spectrographs and of powerful sources of monochromatic illumination. Even so, it is necessary to give long exposures in order to record the fainter details of the spectra with satisfactory intensity. A serious difficulty in such work is the blurring of the spectral lines noticed with prolonged exposures, arising mainly because of the variations in the temperature of the spectrographs and of the dispersing prisms contained in them. The new laboratory and its equipment were

designed with the special aim of eliminating this difficulty as completely as possible.

The new laboratory is a massive structure of granite which faces north and south without any doors or windows on the eastern and western walls. The building contains two large spectrographic rooms, each 30 feet square and 18 feet high, these being separated from each other by a small hall through which they can be entered, by a photometer room and by a dark room for photographic work; entry into the latter can be made through labyrinths connecting them with the spectrographic rooms on either side. Each of the latter is provided with a false roof of thermally insulating material containing apertures which permit of a low-draught ventilation upwards. The windows of the spectrographic rooms face north and south and are set in such a position that no sunlight ever falls on them. Each of the windows is double, the outer one being of glass and the inner of wood. The admission of light and air into the rooms can thus be strictly controlled. With these arrangements, the diurnal variation of temperature within the laboratory was kept at a minimum and the continued operation of mercury lamps within the laboratory did not result in any noticeable fluctuations in temperature.

It was found of advantage to use two spectrographs in the present investigation, both of them being Hilger instruments with quartz prisms and lenses; one of them was the well-known medium size spectrograph of the ordinary or direct type and the other was a large automatic spectrograph of the Littrow type. The smaller instrument was some twenty times as fast as the larger instrument and was therefore to be preferred when the object was to record the fainter details of the spectrum as completely as possible. The larger instrument had a greater resolving power and was therefore more suitable for exhibiting the finer details of the spectrum. However, it suffers from the disadvantage of the so-called " Littrow fog " which sets the limit to the length of exposures which could usefully be given with it. Each spectrograph was placed on a massive teakwood table inside a double-walled box enclosing the instrument completely, the inner walls of the box being of insulating boards and the outer walls of compressed fibre boards impervious to air; the two walls are separated by an air gap. The small aperture through which the slit of the spectrograph was illuminated was closed by a polished plate of quartz. This arrangement successfully prevented any changes in the temperature of the air of the room penetrating through the enclosures into the instrument, so much so that single exposures could be continued as long as desired over several days or even weeks without any blurring of the spectral lines.

3. The Experimental Arrangements

The monochromatic illumination used was the λ 2536·5 resonance radiation of a water-cooled magnet controlled mercury arc in silica, the current being kept well below two amperes. A heavy inductance was introduced in series with the arc to make it stable. It was found much preferable to use, instead of a completely sealed arc, one that was continuously evacuated. It was however necessary to employ an efficient high-speed pump and to run the arc for a sufficient time for the lines due to oxygen and nitrogen of the air to be eliminated before starting an exposure. The water-cooling of the arc was effected internally and only at the mercury pool electrodes, the arrangement being similar to that adopted in the Toronto type of mercury lamps. The most successful type of electrode was one with parallel strands of fine molybdenum wire sealed up by pressure in a narrow tubule of silica and finally closed up by molten lead. The current was led in by copper wires fixed in the lead.

The crystal was illuminated by placing it quite close to the arc, a current of air from a fan being directed against it continuously to prevent it from warming up. The scattered radiations were focussed on the slit of the spectrograph with a quartz lens, suitable apertures being introduced in the path of both incident and scattered radiations to minimise parasitic illumination. Dishes of mercury inside the spectrograph provided enough mercury vapour to filter out the resonance radiation from the scattered light before it reaches the photographic plate. A comparison spectrum of the light of the mercury arc was recorded in each case on the same plate with an exposure sufficient to bring out even the faintest lines.

It should be mentioned that not all crystals of calcite are equally transparent to the λ 2536·5 resonance radiation. The best of the specimens available in the museum of this Institute were used in the present investigation. One of them was a large, flawless and transparent rhomb $3'' \times 2'' \times 2''$ purchased some years ago in New York. A smaller specimen presented by Prof. A. Neuhaus of the Mineralogical Institute of Bonn proved to be of excellent quality and was also used in the research. The advantage of using such clear crystals is that the lines of the mercury arc other than the λ 2536·5 appear only feebly and some of them not at all even in strongly exposed spectrograms. Such of the lines as do appear are readily identified by reference to the comparison spectrum of the mercury arc. The possibility of a mercury arc line being mistaken for a Raman shift or *vice versa* is thereby rendered negligible. The distribution of intensity in the Raman lines along their length is usually different from that of the mercury lines and this is a

further clue which enables them to be distinguished from each other. The analysis of the spectrograms is further facilitated by the extraordinary intensity of the λ 2536·5 radiation in comparison with that of the other lines of the mercury arc run under the conditions employed in the present investigation. Even with the very long exposures given in order to record the faintest Raman shifts, the other lines of the mercury arc do not give observable Raman shifts except in a very few cases. In particular, it has been noticed that the triplet of mercury lines λ 2652·04, λ 2653·68 and λ 2655·13 as well as the line λ 2576·29 do excite the strongest Raman lines observably. As the positions of these lines are exactly calculable, it is easy to locate and eliminate them.

4. General Description of the Results

Five frequency shifts which expressed in wave-numbers are respectively 155, 282, 712, 1086 and 1436 are the most conspicuous features in the Raman spectrum of calcite and were recognized by the earliest investigators, notably Cabannes, Nisi and Rasetti. The three larger frequency shifts arise from the internal vibrations of the CO_3 groups contained in the crystal, while the two smaller frequency shifts arise from the external vibrations of the CO_3 groups which involve translatory and rotatory oscillations of those groups.

We are concerned in the present paper with the study of the various features which make their appearance in the spectra when the exposures are sufficiently prolonged. These changes are most conveniently exhibited in reproductions by recording the spectra with the maximum exposures practicable and then printing them to different depths. The deeper prints exhibit only the most conspicuous features, while in the lighter prints the fainter details are by comparison strongly emphasized. It is found that the reproductions thus obtained represent approximately the effect of varying the original period of exposure of the spectrogram.

Figure 1 (*a*) in Plate IV is a reproduction of a deep print of a spectrogram recorded with our larger instrument by giving an exposure of 100 hours and using a slit-width of 0·05 mm. Fig. 1 (*b*) in the same Plate is a comparison spectrum of the mercury arc. The five principal Raman lines referred to above and their anti-Stokes components are immediately recognized by comparing the two photographs. Fig. 1 (*c*) in the same Plate is a light print of the same spectrogram. It shows various additional features to which we shall return later. A microphotometer record on the scale 1 : 4 of the same spectrogram is reproduced as Fig. 2 in Plate V.

Figure 3 (*a*) and Fig. 3 (*c*) are respectively deep and light prints of a spectrogram recorded with the smaller instrument giving an exposure of

60 hours and using a slit-width 0·04 mm. Taking into account the greater speed of the smaller instrument, this exposure is roughly ten times greater than that used in recording Figs. 1 (*a*) and 1 (*c*) in Plate IV. Under the conditions of the experiment, an exposure of five minutes was found to be sufficient to record all the five Raman lines. Thus, the spectrum reproduced in the Plate represents an exposure 720 times greater than that needed to record what is ordinarily regarded as the Raman spectrum of calcite. Comparing Fig. 1 (*a*) in Plate IV with Fig. 3 (*c*) in Plate VI, it seems almost incredible that they represent one and the same phenomenon. The heavy exposure and the light printing adopted for Fig. 3 (*c*) have evidently resulted in enormously emphasizing the fainter features of the spectrum, while in Fig. 1 (*a*) they are not observable at all. The transition from one extreme to the other can be traced in the sequence from Fig. 1 (*a*) to Fig. 1 (*c*) in Plate IV and then from Fig. 3 (*a*) to Fig. 3 (*c*) in Plate VI. A microphotometer record of the heavily exposed spectrum on the scale 1 : 8 is reproduced as Fig. 4 in Plate VII.

Amongst the phenomena with which we are concerned in the present paper is one of great interest which appears to have been passed over by the earlier investigators without notice, *viz.*, the transformation of the principal Raman shifts from more or less sharply defined lines as recorded with the minimum exposures into bands covering an appreciable range of wavelengths in the strongly exposed spectra. This feature is clearly noticeable in the spectrograms and microphotometer records reproduced in Plates IV, V, VI and VII. The phenomenon is *not* of instrumental origin or due to photographic halation. This is clear from the fact that it is not exhibited by the mercury arc lines of comparable intensity simultaneously recorded in the spectra. The latter do indeed show the well-known photographic spread resulting from prolonged exposures. But this is relatively small and the edges of the lines remain quite sharp. The difference in the behaviour of the lines of the mercury arc and of the principal Raman shifts can be seen very readily by comparing them in the series of four spectra reproduced in Plates IV and VI. It is also evident from a comparison of the microphotometer records reproduced as Fig. 2 in Plate V and Fig. 4 in Plate VII. While there is hardly any difference in the aspect of the mercury arc lines in these two records, there is an enormous difference in the behaviour of the Raman shifts. Fig. 4 in Plate VII exhibits several features which are scarcely, if at all, noticeable in Fig. 2 of Plate V. These, of course, are the fainter features which are recorded in the spectrum only when long exposures are given. The principal Raman shifts which appear in both records also present very different aspects in them. In the record

of the strongly exposed spectrogram they appear broadened out unsymmetrically. This effect is shown by all the five principal Raman shifts but to very different extents. It is only with difficulty observable in the case of the 712 cm.$^{-1}$ shift which might indeed be mistaken for a mercury arc line in this respect. On the other hand, the 1436 cm.$^{-1}$ shift exhibits it very conspicuously. Its unsymmetrical broadening is noticeable even in Fig. 2 of Plate V as will be apparent on comparing its profile with those of the mercury arc lines and is very conspicuous in Fig. 4 of Plate VII. The principal Raman shift of 1086 cm.$^{-1}$ shows the effect conspicuously. It is also exhibited by the low-frequency shifts 155 cm.$^{-1}$ and 282 cm.$^{-1}$; the unsymmetrical broadening of these two lines is evident even in the weakly exposed spectrum and in its photometer record, while in the strongly exposed spectra, the broadening is so large that these two frequency shifts as well as their anti-Stokes components seem to run into each other and form an apparently continuous band of illumination.

We may interpret these phenomena by describing them as due to satellite radiations which accompany the principal Raman lines and represent shifts of frequency differing from them by relatively small amounts. The unsymmetrical character of the broadening indicates that the frequency shifts of the satellite radiations are for the most part smaller than those of the Raman lines which they accompany. The intensity of the satellite radiations is of course very small and this is indicated by the very long exposures needed to record them.

5. The Principal Raman Shift with its Satellites and Overtones

Light is thrown on the nature and origin of the phenomenon referred to above by a critical study of the principal Raman frequency shift of 1086 cm.$^{-1}$ arising from the totally symmetric internal vibrations of the CO_3 ion and the accompaniments of that line. Rasetti in his investigation made with an instrument similar to our smaller spectrograph, observed and reported that the principal frequency shift of 1086 cm.$^{-1}$ is accompanied by a frequency shift of 1067 cm.$^{-1}$ to which he assigned an intensity zero as compared with an intensity fifty for the main line. In the present investigation, it has been noted that the spectrogram recorded with the smaller instrument and a fine slit exhibits, besides the frequency shift of 1067 cm.$^{-1}$ recorded by Rasetti, another and much fainter line clearly resolved from it and further removed from the principal frequency shift. This component has been proved by exact measurement to be the 1086 cm.$^{-1}$ shift excited by radiation of wave-length λ 2534·8 which appears as a companion of the resonance radiation of wave-length λ 2536·5. The features referred to above are

indicated by inflexions in the microphotometer record on the scale 1 : 8 reproduced as Fig. 4 in Plate VII. But they are seen much more clearly in the microphotometer record on the much larger scale of 1 : 50 reproduced as Fig. 6 in Plate IX. The unsymmetrical broadening of the principal Raman shift is very conspicuously exhibited by that record.

The greater dispersion and resolution of the larger spectrograph used in the present investigation has proved itself invaluable in revealing the true characters of the phenomenon now under consideration. In the spectrogram, obtained with that instrument and reproduced as Fig. 1 (*c*) in Plate IV the features mentioned above are both recognizable. They are however shown far more clearly in the greatly enlarged picture of a part of the same spectrogram reproduced as Fig. 5 (*b*) in Plate VIII. The extreme sharpness and discrete character of the 1067 cm.$^{-1}$ shift is clearly shown in that reproduction. The sharpness of the 1086 cm.$^{-1}$ shift given by the radiation λ 2534·8 of the mercury arc also seen in that picture is noteworthy as it serves to emphasize the real monochromatism of the Raman shift given by crystals as recorded with small exposures. The microphotometer record on the scale 1:4 of the same spectrogram reproduced as Fig. 2 exhibits these features recognizably. But a microphotometer record on a much larger scale is needed to disclose the finer features of the phenomenon. Such a record on the scale 1:50 is reproduced as Fig. 1 in the text.

The principal peak corresponding to the frequency shift of 1086 cm.$^{-1}$ and the clearly separated subsidiary peak with a shift of 1067 cm.$^{-1}$ are both conspicuous features in the record. Intermediately between these peaks, the photometer curve exhibits two inflexions in its course which correspond to frequency shifts of 1072 cm.$^{-1}$ and 1075 cm.$^{-1}$ respectively. The reality of these inflexions has been confirmed by taking microphotometer records at different points along the same spectral line and also with spectrograms recorded with different exposures.

The results of the investigation may thus be stated as follows: The principal Raman frequency shift of 1086 cm.$^{-1}$ is accompanied by *three* satellites having frequency shifts of 1067 cm.$^{-1}$, 1072 cm.$^{-1}$ and 1075 cm.$^{-1}$ respectively. The reason why the two latter are less conspicuous than the first is evidently because that they are closer to the principal shift recorded with much greater intensity and are therefore less clearly resolved from it than the component differing from it in frequency to the greatest extent. Taking the observed facts at their face value, we may explain the appearance of these three satellites as due to independent discrete normal modes of vibration of the structure of the crystal, which, though Raman-inactive in the first

approximation, are rendered feebly active by reason of their proximity in frequency to the strongly active mode of frequency 1086 cm.$^{-1}$ and presumably also by reason of their possessing certain features of resemblance to it in their respective modes of vibration.

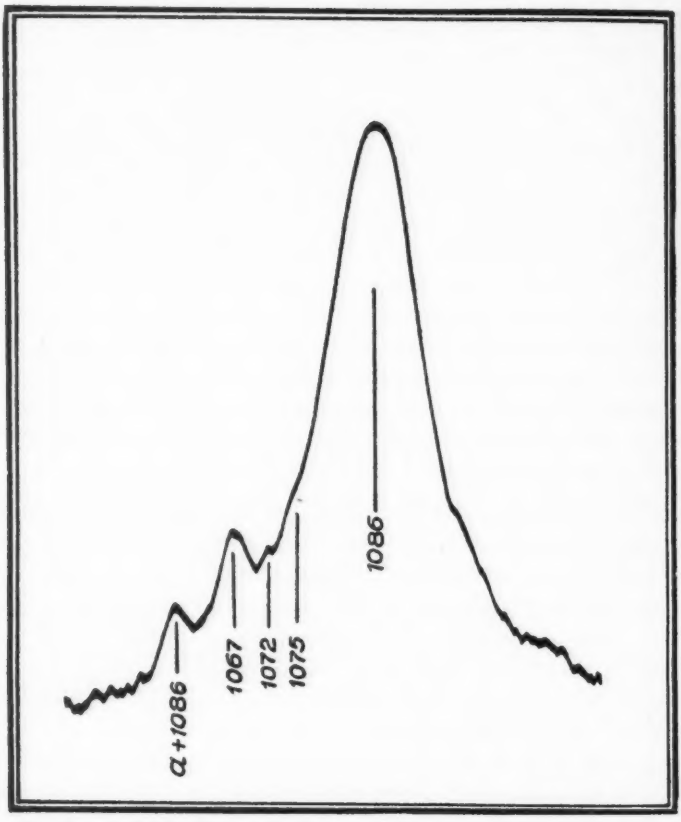


FIG. 1. Enlarged microphotometer record showing the 1086 cm.$^{-1}$ line and its satellites.

The foregoing conclusions receive striking support in the features observable in the strongly exposed Raman spectra in the vicinity of double the frequency shifts under consideration, *viz.*, in the region displaced from the exciting radiation by shifts lying between the range 2172 cm.$^{-1}$ and 2134 cm.$^{-1}$ Shifts of this magnitude would be recorded near the end of the reproduced spectrograms furthest from the exciting radiation. They can

be seen very clearly not far from the last mercury line in Fig. 3 (*a*) in Plate VI. We observe a *sharply defined line* with a frequency shift of 2173 cm.$^{-1}$; and separated from this by a dark region appears a diffuse line of comparable intensity having its peak of intensity at 2148 cm.$^{-1}$ These features are also shown in the spectrum as recorded with the larger instrument and reproduced as Fig. 1 (*c*) in Plate IV. The frequency shift of 2173 cm.$^{-1}$ here appears as a needle-sharp line in striking contrast with the diffuseness of the line clearly separated from it and having its maximum of intensity at a frequency shift of 2148 cm.$^{-1}$ The microphotometer records reproduced as Fig. 2 in Plate V and Fig. 4 in Plate VII exhibit these features quite clearly. The differences in the character of the two microphotometer records arise from the great difference in the photographic exposures and of the resolving powers of the two instruments employed. A microphotometer record on the greatly enlarged scale of 1 : 50 showing these features is reproduced in the text as Fig. 2.

The sharp line with a frequency shift of 2173 cm.$^{-1}$ is clearly the octave of the principal Raman frequency shift of 1086 cm.$^{-1}$ The diffuse line with its peak at 2148 cm.$^{-1}$ is explicable as arising from the superposition of the octaves of a number of discrete normal modes whose frequencies are *less* than 1086 cm.$^{-1}$, the lowest of them being 1067 cm.$^{-1}$ and the two others having higher values. These normal modes, being inactive, manifest themselves only very weakly as fundamentals. But theory indicates they would be Raman-active as octaves to the same extent as the active fundamental of 1086 cm.$^{-1}$ The fact that the band centred at 2148 cm.$^{-1}$ is of comparable intensity with the line at 2173 cm.$^{-1}$ thus receives a natural explanation.

6. The Origin of the Satellite Radiations

The frequency shifts observed in the Raman effect arise from the excitation of the normal modes of vibration of the atoms in the structure of the crystal about their positions of equilibrium by the incident radiation. In the determination of these modes and their frequencies, it is usual to consider those modes which can be regarded as characteristic of the groups of atoms included in the unit cells of the crystal structure. If the unit cell contains p atoms, the number of such normal modes of vibration would evidently be $(3p - 3)$, the three excluded degrees of freedom representing the three translations of unit cell. But this way of dealing with the matter is obviously not complete or satisfactory. If we define a normal mode as one in which the atoms in a crystal vibrate with the same frequency and in the same or opposite phases, it can be readily shown to be a consequence of its three-dimensional periodicity of structure, that a crystal has $(24p - 3)$ normal

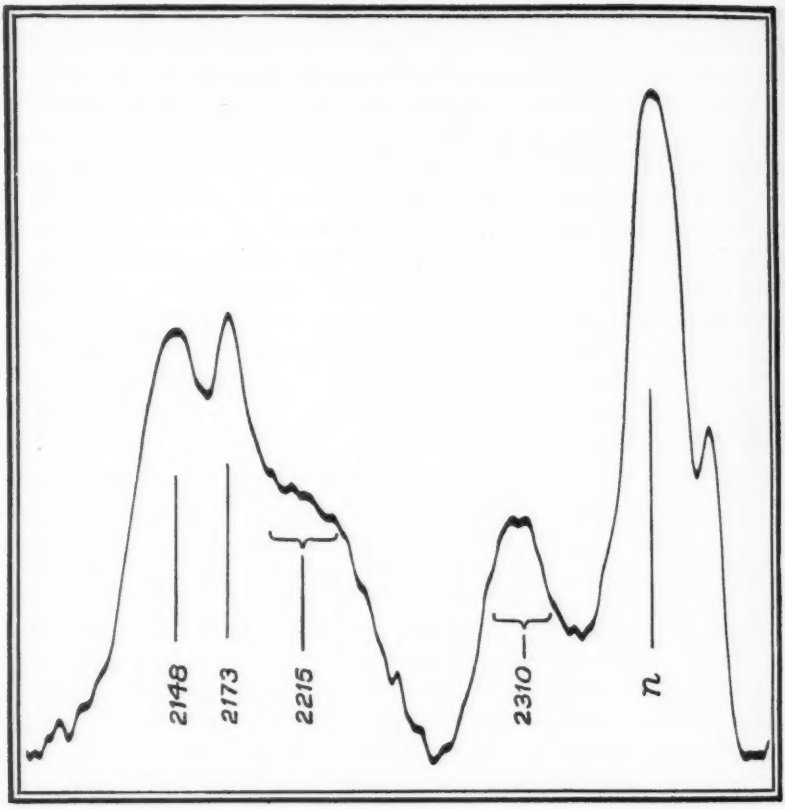


FIG. 2. Enlarged microphotometer record showing the overtone of the principal Raman shift and other features.

modes of vibration, each of which is characterised by a definite monochromatic frequency. In $(3p - 3)$ of these normal modes, equivalent atoms in adjacent cells of the structure have the same amplitude and the same phase of vibration, while in the remaining 21 p modes they have the same amplitudes of vibration but their phases are opposite along one, two or all the three axes of the crystal structure. The latter may be briefly designated as the superlattice vibrations.

We may proceed to consider the consequences of the foregoing proposition in the case of calcite. We shall confine our attention at first to the modes involving the totally symmetric internal vibrations of the CO_3 group. Each

unit cell of the crystal structure contains two such groups which are non-equivalent, the phases of vibration of which in any normal mode may be either the same or opposite. There are eight different situations regarding the relative phases of vibration in the unit cells of the crystal adjoining each other along the three axes of the structure. Thus, in all, there are 8×2 or sixteen possible kinds of normal modes involving the totally symmetric vibration of the CO_3 groups. The rhombohedral symmetry of the crystal however makes the two axes perpendicular to the trigonal axis equivalent to each other, thereby reducing the number of distinct normal modes from sixteen to eight only. A further simplification becomes possible when we note that the equivalent CO_3 groups located along the trigonal axes are remote from each other in comparison with their relative distances along the two other axes of the crystal. Hence, we may ignore the additional possibilities arising from the reversal of phase of their vibrations along the trigonal axis. The number of *effectively* different normal modes is reduced thereby from eight to four. The mode that is Raman-active would obviously be the one in which any one CO_3 group has the same phase of vibration as all the other groups in its neighbourhood. In each of the three other normal modes, half the number of CO_3 groups vibrate in one phase and the other half in the opposite phase and hence they would be Raman-inactive in the first approximation.

It is evident also that the frequencies of the four normal modes indicated by the foregoing considerations would not be identical. For, these frequencies which are principally determined by the internal forces arising within each group would also be influenced by the interactions between similar groups vibrating with the same frequency in the neighbourhood and such interactions would be altered by a reversal of their relative phases. The order of magnitude of the differences in frequency arising in this manner is indicated by the well-known fact that while the frequency shift as observed in the crystal is 1086 $cm.^{-1}$, a similar vibration in solutions containing CO_3 ions gives a frequency shift of only 1065 $cm.^{-1}$

As already indicated, the strongly Raman-active vibration in calcite gives a frequency shift of 1086 $cm.^{-1}$ which corresponds to the case in which all the CO_3 groups vibrate in identical phases. Hence, the three other modes in which half of them vibrate in opposite phases may be expected to be of lower frequencies. Though, as already stated they would be Raman-inactive in the first approximation, various considerations indicate that they would be rendered feebly active by reason of the general similarity in the character of their vibrations and their close approximation in frequency to the strongly active mode.

We have seen in the preceding section that in the strongly exposed Raman spectra, the frequency shift of 1086 cm.$^{-1}$ is accompanied by weak satellites with lower frequency shifts which are respectively, 1075, 1072 and 1067 cm.$^{-1}$ Further, these satellites manifest themselves as octaves quite as strongly as the octave of the 1086 cm.$^{-1}$ frequency. These facts are in such excellent agreement with the theoretical considerations set forth above as to leave no doubt regarding the correctness of the explanation. It is also easy to understand why the 1086 cm.$^{-1}$ frequency exhibits the phenomenon of the satellites in such a clear and conspicuous manner. Being itself an extremely intense line, the satellites which derive from it have observable intensities and being themselves also sharp are seen resolved from it when a spectrograph of adequate power is brought to bear on them.

7. SATELLITES AND OVERTONES OF OTHER FREQUENCY SHIFTS

Besides the three modes of internal vibration of the CO_3 groups appearing as frequency shifts in the Raman spectrum, there is still another in which the carbon and oxygen atoms in these groups oscillate in opposite phases along the trigonal axis of symmetry. Theory indicates that such an oscillation would be infra-red active but would not give a Raman shift of the same frequency, though it might give one with double that frequency. These indications of theory are in agreement with observation. A sharply defined maximum located at 877 cm.$^{-1}$ is observed in the infra-red absorption by thin layers of very finely powdered calcite. *Per contra*, no frequency shift in that vicinity is observable even in the most strongly exposed Raman spectra. Cabannes, Nisi and others noticed and recorded a sharp line with a frequency shift of 1749 cm.$^{-1}$ in the Raman spectrum of calcite. This is clearly identifiable as the octave of the mode of vibration referred to above. Fig. 5 (*c*) in Plate VIII recorded with the λ 4358 excitation exhibits this frequency shift with a notable intensity. In the excitation by λ 2536·5, the same frequency shift appears as a line falling between the second and third components of the triplet in the spectrum of the mercury arc; though it can be observed in that position, a detailed investigation is difficult. So far as is ascertainable, the frequency shift is a single line not accompanied by any satellites or companions.

As already reported in an earlier section, the frequency shift of 1436 cm.$^{-1}$ conspicuously exhibits an unsymmetrical broadening in strongly exposed spectra. In the microphotometer record reproduced in Fig. 2 of Plate V, three satellites can be recognized whose frequency shifts are respectively 1399, 1412 and 1418 cm.$^{-1}$ In the microphotometer record of the more heavily exposed spectrum reproduced in Fig. 4 of Plate VII, the unsymmetrical

broadening is clearly visible but the satellites are not resolved from the parent line. Their presence however is clearly indicated in the record obtained on a larger scale 1 : 50 and reproduced below as Fig. 3 in the text.

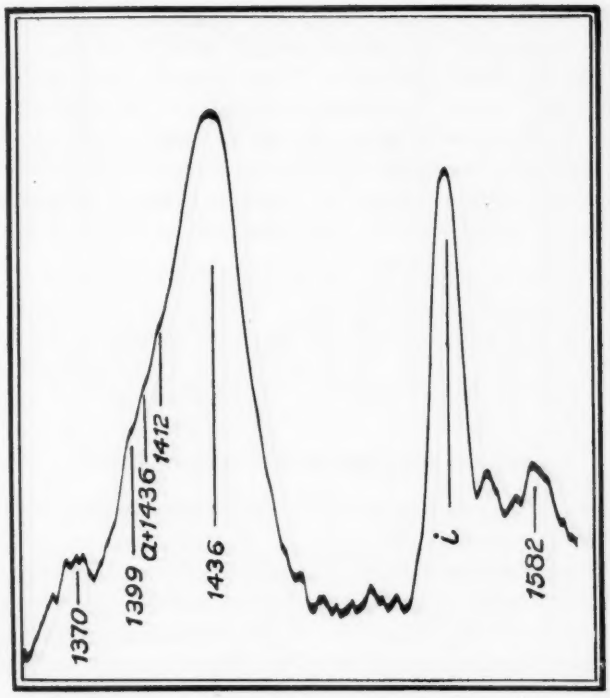


FIG. 3. Enlarged microphotometer record showing 1436 cm.$^{-1}$ line and other features.

In Fig. 4 (Plate VII), the positions where the octaves of the 1436 cm.$^{-1}$ shift and of its satellites appear are indicated in the microphotometer record. They fall on and near the triplet of Raman lines having a common frequency shift of 1086 cm.$^{-1}$ excited by the triplet of the mercury arc and this makes it difficult to describe them completely. It is evident, however, that the intensity of the overtones of 1436 cm.$^{-1}$ and its satellites is very small compared with the intensity of the octaves of the 1086 cm.$^{-1}$ and of its satellites. The enlarged microphotometer record reproduced in the text as Fig. 4 however makes it clear that the satellites of the 1436 cm.$^{-1}$ shift manifest themselves as octaves no less conspicuously than their parent line.

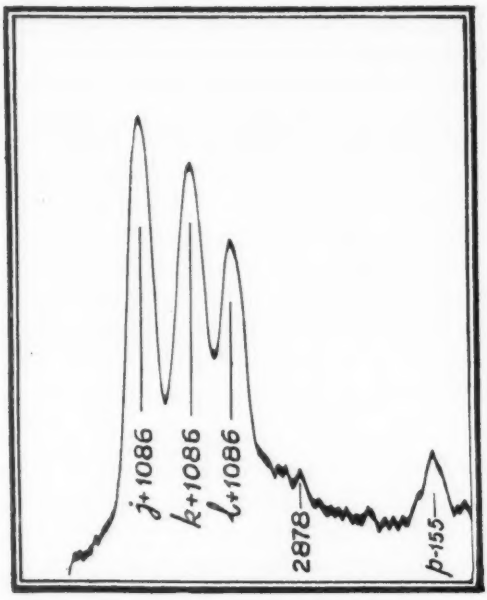


FIG. 4. Enlarged microphotometer record showing the overtones of 1436 cm.$^{-1}$ line and of its satellites.

The 712 cm.$^{-1}$ frequency shift is much less intense than the 1436 cm.$^{-1}$ and its unsymmetrical broadening is barely perceptible. The microphotometer record reproduced as Fig. 6 in Plate IX however shows a weak companion which may be interpreted as a satellite line with a frequency shift of 685 cm.$^{-1}$ It is however difficult to exclude the possibility that this may be only the 712 cm.$^{-1}$ shift excited by the weak λ 2534·8 line of the mercury arc.

The octave of the 712 cm.$^{-1}$ frequency may be expected to be extremely weak. Even otherwise, it could scarcely be expected to be observable, since it would overlap the 1436 cm.$^{-1}$ shift in the spectra recorded with the necessary exposures.

8. THE LOW-FREQUENCY SPECTRUM

We now proceed to consider the characters of the Raman spectrum in the region of the smaller frequency shifts (< 600 cm.$^{-1}$). The most conspicuous features in this region are of course the frequency shifts of 155 cm.$^{-1}$ and 282 cm.$^{-1}$, the latter being much the stronger of the two. They have been identified as arising from the translatory oscillations of the CO_3 groups in their own plane combined with rotational oscillations about an axis also lying

in that plane. The two other types of oscillation of the CO_3 groups which are possible are translations along the trigonal axis and rotations also about the same axis. Theory indicates that such oscillations would be Raman-inactive. The question however arises whether movements of the latter two types might not in the second approximation exhibit themselves weakly as frequency shifts. The answer to this question appears to be in the affirmative. Cabannes in his earliest studies noticed and recorded a line in the spectrum with a frequency shift of 221 cm.$^{-1}$ The reality of this has been definitely established by the present investigation. It is visible as a sharp line between the two strong Raman lines in the spectrograms reproduced as Fig. 1 (*c*) in Plate IV and Fig. 5 (*a*) in Plate VIII. It also manifests itself conspicuously as peaks on both sides of the exciting radiation in the microphotometer record of the same spectrogram as Fig. 2 of Plate V.

Various considerations indicate that the frequency shift of 221 cm.$^{-1}$ the reality of which is thus definitely established represents the normal mode in which the CO_3 groups in the crystal oscillate in a direction normal to their planes, neighbouring layers of the CO_3 groups periodically approaching and receding from each other, the layers of Ca ions intermediate between them remaining at rest. The frequency of such an oscillation may be expected to be that actually observed. Confirmatory evidence of the correctness of this explanation of the 221 cm.$^{-1}$ shift of frequency comes to hand from a comparison of the low-frequency Raman spectra of calcite and aragonite. There are striking resemblances and also noteworthy differences between the two spectra, these being evidently consequences of the close similarities as well as the specific differences in the structures of the two crystals. Modes of oscillation of the CO_3 groups similar to those now under consideration are Raman-active in aragonite by reason of its lower symmetry of structure. Indeed, a close group of lines with an average frequency shift of 215 cm.$^{-1}$ and having a notable intensity is a very striking feature in the spectrum of aragonite.

Hibben in his book reports having observed frequency shifts of $\pm$ 86 cm.$^{-1}$ in the Raman spectrum of calcite. Some support for this claim is forthcoming in the present investigation, though the matter has not been placed completely beyond doubt. The rotational oscillation of the CO_3 groups about the trigonal axis of symmetry might be expected to have a frequency of that order of magnitude.

We may now briefly comment upon the explanation of the behaviour of the two principal Raman shifts in this region in strongly exposed spectra already described earlier in the present paper. Dynamical theory indicates that the unit cell in the calcite structure consisting of two CO_3 groups and two

Ca ions intervening between them has ten different normal modes of vibration. If the alternations in the phase of the vibration in adjacent unit cells along the three axes of the structure are also taken into account, this number would be increased to forty in all. The additional thirty modes would have frequencies different from those of the corresponding modes in the group of ten first referred to. Only two out of these forty modes would, strictly speaking, be Raman-active. But it appears inevitable that when one or the other of these two modes is excited, other modes approximating to them in frequency would also be excited, though only very feebly. The spectrum consisting of such a crowd of satellite radiations with different frequencies would naturally appear more or less continuous and this is what is actually observed.

The nature of the vibrations now under consideration is such that we could scarcely expect them to exhibit overtones with any notable intensities, and indeed no evidence is forthcoming of such overtones as *discrete* frequency shifts in the region under consideration. But we do observe a weak band of illumination in the spectrum covering the whole range of frequency shifts upto 600 $cm.^{-1}$ This may be regarded as a superposition of the effects arising from all the forty possible normal modes of vibration.

9. COMBINATIONAL FREQUENCY SHIFTS

We proceed to consider and report on the various features observed in the strongly exposed Raman spectra of calcite other than those already discussed above. It appears desirable to make some comments of a general nature regarding the principles on which the interpretations suggested are based. It is essential in the first place to make the most accurate measurements of the frequency shifts proposed to be interpreted as well as of the frequency shifts to which they might be related as overtones or combinations. It is not possible, however, to base interpretations solely on arithmetical agreements, as the latter might be purely fortuitous. Nor is it permissible to base the interpretations entirely on the selection rules which have been proposed on theoretical grounds. Frequency shifts might be permitted by those rules and yet be unobservable by reason of vanishingly small intensity or other circumstances. Further, the selection rules themselves rest on certain assumptions and are therefore not necessarily valid in all cases. In view of these remarks, it is important that other factors are also taken into consideration. The intensity and spectral character of the frequency shifts are factors of particular importance in this respect. These remarks are made, since the reservations which they imply have been overlooked in several

instances in the earlier literature and assignments have been proposed which are wholly unacceptable.

An examination of the strongly exposed spectra and of their microphotometer records reveals numerous features calling for explanation. After a careful review of the various possibilities, we find the most reasonable interpretation to be that they arise from combinations of the various normal modes of vibrations of the unit cells in the crystal structure with the two normal modes having frequencies respectively of 1086 and 875 cm.$^{-1}$ The former is the totally symmetric oscillation of the CO_3 groups which gives by far the most intense line in the Raman spectrum, while the other is an infra-red active mode which gives a Raman shift of double its frequency with notable intensity. We find it possible in the manner indicated to explain practically every one of the observed features in the spectrum. Table I gives a

TABLE I

Observed frequency shifts: Their characters and suggested origins

1186 cm.$^{-1}$	Diffuse and weak	1086+ 100 cm.$^{-1}$
1241 ,,	Sharp and weak	1086+ 155 ,,
1275 ,,	Diffuse and very weak	1086+ 189 ,,
1305 ,,	Sharp and very weak	1086+ 221 ,,
1370 ,,	Sharp and strong	1086+ 282 ,,
1795 ,,	Sharp but weak	1086+ 712 ,,
2522 ,,	Indication only	1086+1436 ,,

list of the combinations of the first kind and Table II a list of the combinations of the second kind. It is significant that while the octaves of the two frequencies 1086 and 875 cm.$^{-1}$ are conspicuous features in the Raman spectrum, no frequency shift in the vicinity of 1961 cm.$^{-1}$ which would represent a summation of them is observable even in the most strongly exposed spectra. This is readily understood, since the atomic vibrations in these two modes occur in mutually perpendicular directions and that while one of them is totally absent in the infra-red absorption spectrum, the other is conspicuously present.

The following comments may be offered on the entries in Table I. That the strongly Raman-active frequency 1086 cm.$^{-1}$ would combine with other

strongly Raman-active frequencies, *viz.*, 155, 282, 712 and 1436 cm.$^{-1}$ to give sharply defined summational shifts is only to be expected. That the strongest of them is also the combination with the strongly active 282 cm.$^{-1}$ is also intelligible. That no summations appear in Table I corresponding to the strongly infra-red active normal modes with frequencies 330 and 357 cm.$^{-1}$ might have been anticipated on theoretical grounds. The corresponding summations, *viz.*, 1416 and 1443 cm.$^{-1}$ would in any event, however, have been unobservable owing to their overlap with the strong 1436 cm.$^{-1}$ Raman shift. Table I also records summations with three other low frequencies, *viz.*, 100, 189 and 221 cm.$^{-1}$, the former two as weak and diffuse lines and the latter as a weak but sharp line. The first two frequencies are presumably to be identified with two normal modes which are infra-red active, while the 221 cm.$^{-1}$ represents a normal mode which itself appears weakly as a Raman shift and the nature of which has been discussed earlier in this paper.

In strong contrast with the entries in Table I, the frequency shifts listed in Table II appear in most cases as diffuse bands but with notable intensities. The two bands of lowest frequency are respectively a summational and a differential, the former being the more intense of the two, the frequency involved being in either case 84 cm.$^{-1}$ As remarked earlier in the paper, this frequency probably represents the rotational oscillations of the CO_3 groups in their own plane. The appearance in Table II of summations with the Raman-active frequencies of 155 and 282 cm.$^{-1}$ is very surprising, but there is no question as to their reality, since they are recorded with notable intensities and no alternative explanation of these features is forthcoming. Here, as in three other cases listed in Table I, there is a clear-cut violation of the selection rules of which the explanation must be left an open question. The other frequencies of which the summations are listed in Table II are those manifesting themselves strongly in infra-red absorption. Investigators in the latter field are agreed that the maximum which appears in nearly the same position as the Raman frequency shift of 712 cm.$^{-1}$ is a sharply defined one. It is therefore not surprising that the corresponding summation listed in Table II also appears as a strong sharp line. The position is however different with regard to the last two summations appearing in the table. Hunt and collaborators who have investigated the infra-red absorption by a very thin layer of powdered calcite record a peak at 1439 cm.$^{-1}$, but this is only the crest of a very broad maximum and it is therefore not surprising that the corresponding summation appears in Table II as a diffuse band. Perhaps the most remarkable entry in the table is that of the extremely diffuse band which corresponds to a summation with an infra-red absorption band having a maximum at 1340 cm.$^{-1}$ There is no place for such a frequency in the scheme of normal

TABLE II

Observed frequency shifts : Their characters and suggested origins

794 cm.$^{-1}$	Diffuse and weak	875− 84 cm.$^{-1}$
957 ,,	Diffuse and strong	875+ 84 ,,
1025 ,,	Diffuse and strong	875+ 155 ,,
1159 ,,	Diffuse and strong	875+ 282 ,,
1207 ,,	Diffuse and weak	875+ 330 ,,
1232 ,,	Sharp and weak	875+ 357 ,,
1582 ,,	Strong and sharp	875+ 706 ,,
2215 ,,	Diffuse and strong	875+1340 ,,
2310 ,,	Diffuse and strong	875+1439 ,,

modes of vibration of the unit cell of the calcite structure. The suggestion may therefore be hazarded that this band is a satellite or an aggregate of satellites accompanying the infra-red absorption at 1439 cm.$^{-1}$ but distinctly separated from it and analogous to the satellites accompanying the 1436 cm.$^{-1}$ Raman frequency shift already discussed. This suggestion, it may be remarked, is strongly supported by the shape of the absorption curve reproduced in the paper by Hunt and collaborators. Their diagram shows that the absorption of which the crest appears at 1439 cm.$^{-1}$ is of a highly unsymmetrical shape; it rises steeply from nearly perfect transmission at 1650 cm.$^{-1}$ to almost complete opacity at 1439 cm.$^{-1}$ and then drops down quite gradually to nearly perfect transmission again only at 890 cm.$^{-1}$

In conclusion the author wishes to express his sincere thanks to Prof. Sir C. V. Raman, F.R.S., N.L., for the keen interest he took in this investigation and for the valuable suggestions that he gave for the preparation of this paper.

10. SUMMARY

The paper reports the results of a study of the Raman spectrum of calcite recorded with prolonged exposures.

(*a*) The principal Raman shift of 1086 cm.$^{-1}$ is accompanied by much weaker satellites whose frequency shifts are 1067, 1072 and 1075 cm.$^{-1}$ The octave of the principal mode is recorded as a sharp line with a frequency shift

of 2173 cm.$^{-1}$ with a diffuse companion of comparable intensity which is a superposition of the octaves of the three satellites. The 1436 cm.$^{-1}$ Raman shift likewise has satellites at 1399, 1412 and 1418 cm.$^{-1}$ and its octave is feebly recorded as a sharp line, while the octaves of the satellites are also observed in its vicinity. The origin of the satellite radiations is discussed and it is shown that they represent the superlattice vibration frequencies of the calcite structure which are feebly excited.

(*b*) The appearance of a sharp Raman line with a frequency shift of $\pm$ 221 cm.$^{-1}$ is confirmed and it is shown to arise from a normal mode usually considered as inactive.

(*c*) The two intense Raman shifts of 155 and 282 cm.$^{-1}$ exhibit a highly unsymmetrical broadening, as also wings of low intensity spread out over the whole range of frequency shifts between $-$ 300 cm.$^{-1}$ to $+$ 600 cm.$^{-1}$ This spectrum is explicable as arising from a very feeble excitation of the whole group of forty lattice and superlattice frequencies of the calcite structure and their overtones and combinations.

(*d*) Sixteen combinational frequency shifts have been recorded. Seven of them are explained as combinations with the 1086 cm.$^{-1}$ Raman line and the the nine others as combinations with 875 cm.$^{-1}$ Some of the observed combinations violate the selection rules.

REFERENCES

The literature on the Raman spectrum of calcite and its theoretical interpretation is very extensive. Only the papers which have been referred to in the text and which have a bearing on the results of the present investigation are quoted below.

1. Bhagavantam and Venkatarayudu — *Proc. Ind. Acad. Sci.*, 1939, **9 A,** 224.
2. Cabannes, J. .. *Comptes Rendus*, 1929, **188,** 1041.
3. Couture, L. .. *Annales de Physique*, 1947, **2,** 5.
4. Hunt, Wishard and Bonham .. *Analyt. Chem.*, 1950, **22,** 1478.
5. Krishnan, R. S. .. *Proc. Ind. Acad. Sci.*, 1945, **22 A,** 182.
6. Nisi, H. .. *Proc. Imp. Acad. Tokyo*, 1929, **5,** 127.
7. Rasetti, F. .. *Nuovo Cimento*, 1932, **9,** 72.
8. Went, J. .. *Doctorate Thesis*, 1935, Utrecht.
9. Hibben, J. H. .. *Raman effect and its chemical applications*, 1939, pp. 428.

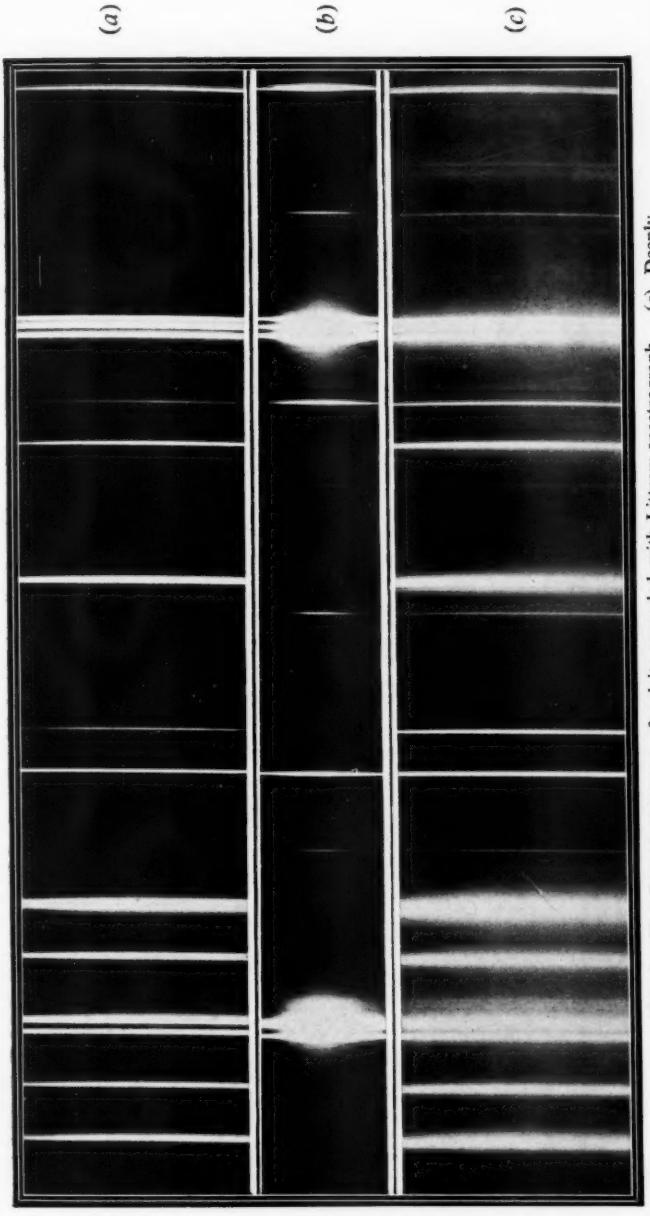


FIG. 1. The Raman spectrum of calcite recorded with Littrow spectrograph. (*a*) Deeply printed, (*b*) Spectrum of the mercury arc, (*c*) Lightly printed.

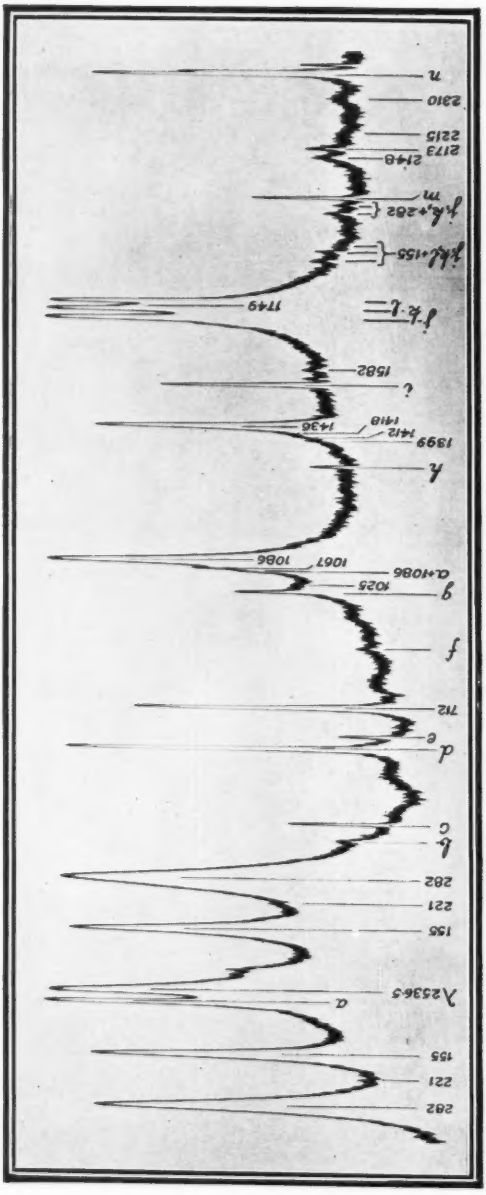


FIG. 2. Microphotometer record of the Raman spectrum of calcite recorded with the Littrow spectrograph.

Note.—The numbers denote the Raman shifts in cm.$^{-1}$ while *a*, *b*, *c*, etc., refer to the mercury arc lines.

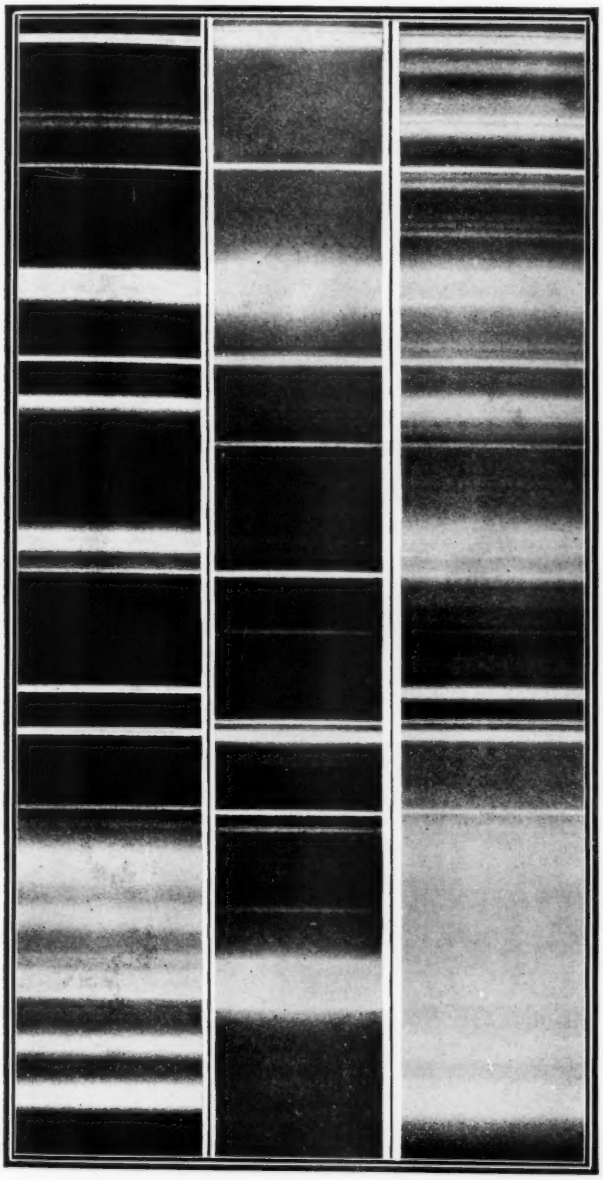


FIG. 3. The Raman spectrum of calcite recorded with the medium quartz spectrograph.
(*a*) Deeply printed, (*b*) Spectrum of the mercury arc, (*c*) Lightly printed.

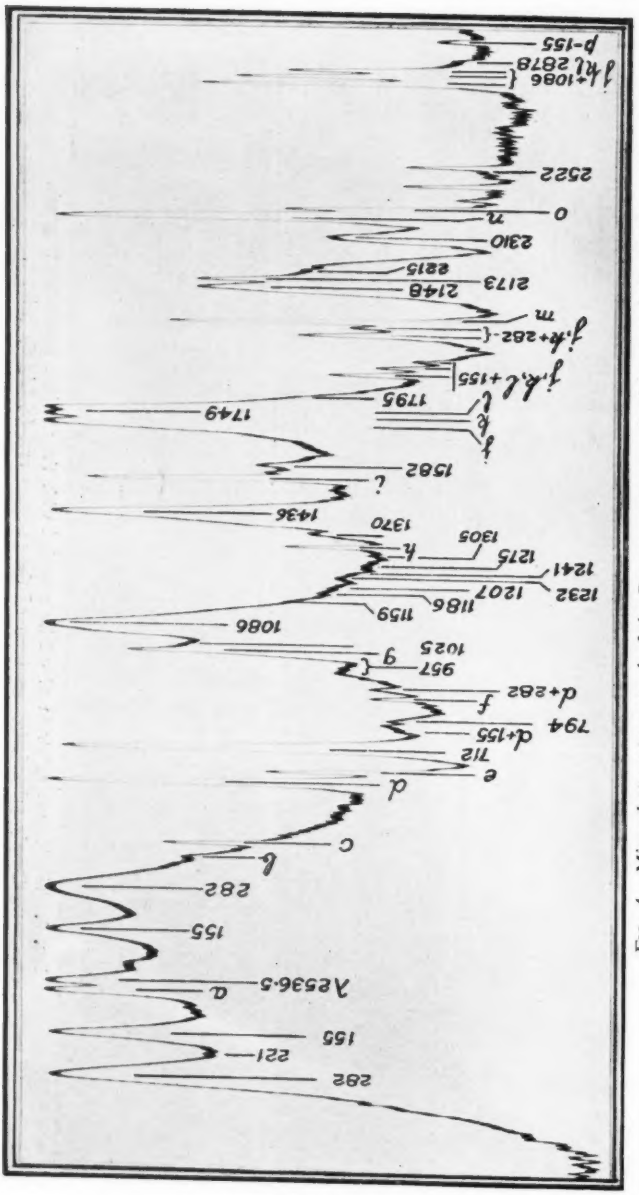


FIG. 4. Microphotometer record of the Raman spectrum of calcite recorded with the medium quartz spectrograph.

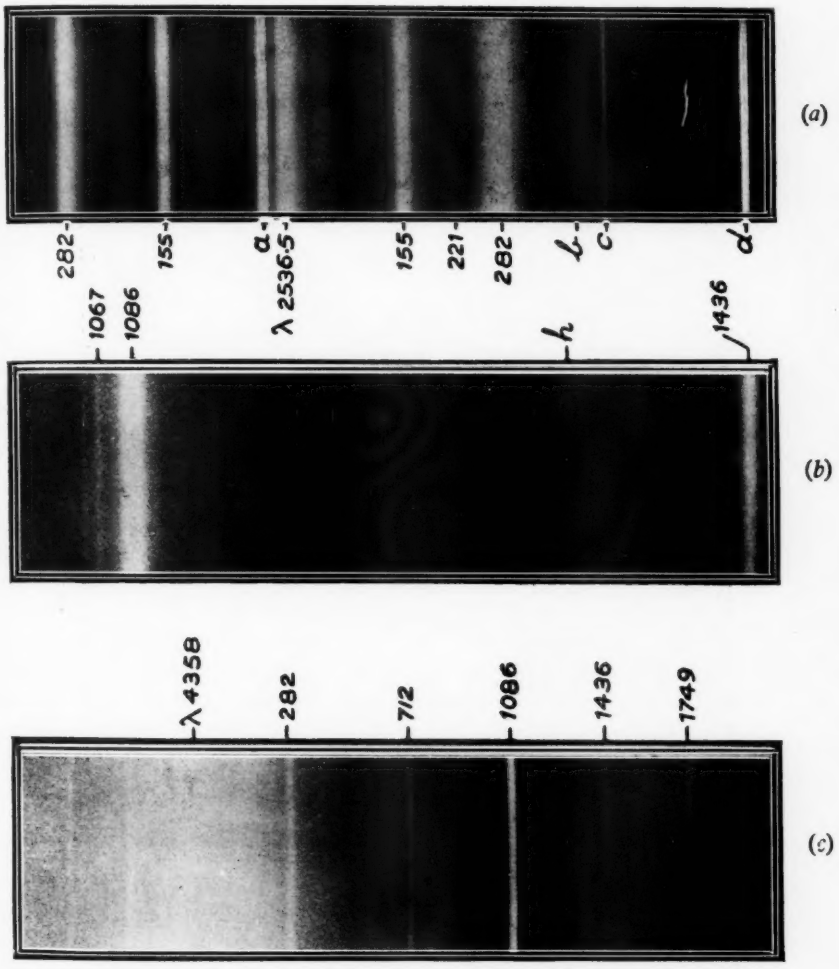


FIG. 5. The Raman spectrum of calcite; (*a*) and (*b*) Enlargements of some portions of Fig. 1 (*c*); (*c*) Spectrum recorded with λ 4358 excitation.

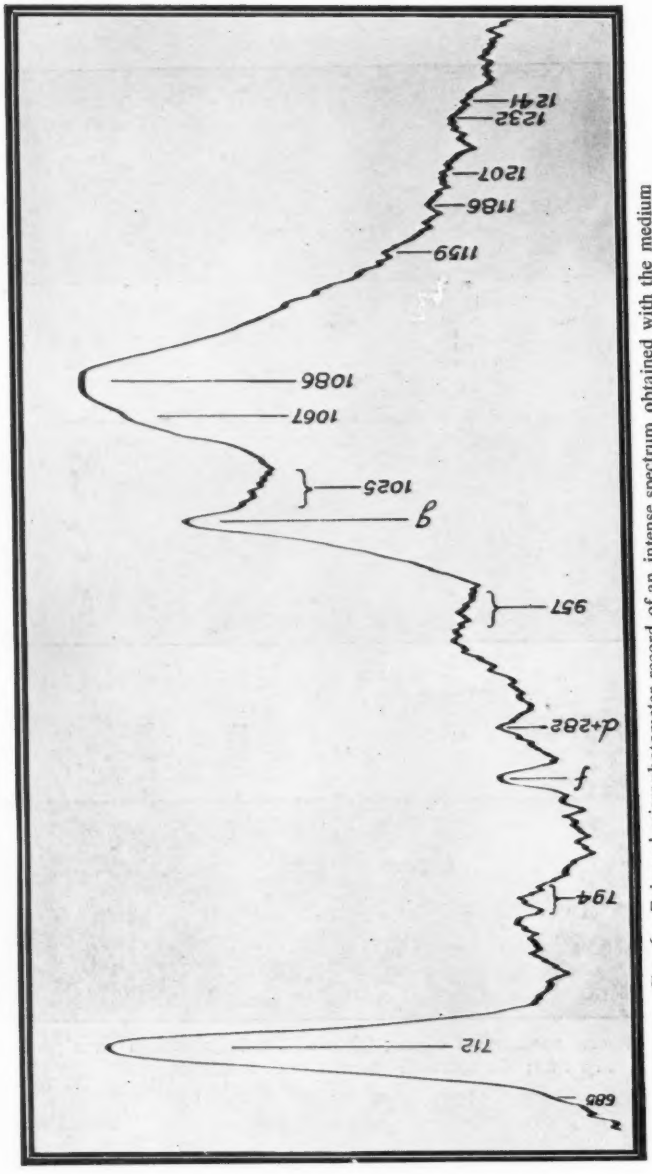


FIG. 6. Enlarged microphotometer record of an intense spectrum obtained with the medium quartz spectrograph.

THE THEORY OF THE ANHARMONIC OSCILLATOR

By K. S. Viswanathan, F.A.Sc.

(*Memoir No. 97 of the Raman Research Institute, Bangalore-6*)

Received May 22, 1957

1. Introduction

Anharmonicity of vibration plays an important role in several branches of physics. Its importance was first recognised in acoustics[1]; the presence of overtones of the fundamental mode of a tuning fork and the alteration of its pitch with intensity changes were successfully accounted for as the effects of the anharmonicity of the oscillator. More recently, the subject has acquired a fresh interest in relation to the subject of molecular spectroscopy.[2] The thermal expansion[3] of crystals also owes its origin to the anharmonic nature of the vibrations inside a crystal lattice.

It is the object of the present note to give an exact treatment of the classical problem of the anharmonic oscillator and also to draw attention to certain of its features which by an appeal to the Correspondence Principle lead to the results of wave mechanics. In Section 2, exact expressions have been given for the shift in the mean position of the oscillator from the origin, its frequency and the amplitudes of the different harmonics. In section 4, the eigenvalues of the oscillator are determined by using the W.K.B. method. It is shown that these are the solutions of a transcendental equation involving elliptic functions and that the first correction to any energy level of the system from its harmonic oscillator value is identical with the one obtained from the perturbation theory.

2. The Classical Problem

Let m denote the mass of the oscillator and x be its displacement. The potential energy of the system may be expressed as

$$V = \tfrac{1}{2}k_1x^2 + \frac{1}{3!}k_2x^3. \qquad (1)$$

We stop with the cubic term of the expansion since this is sufficient to explain most of the observed features of the spectra of diatomic molecules. Further, we take the constant k_2 to be negative in accordance with the conventions of molecular spectroscopy.

The equation of conservation of energy for the oscillator is

$$\tfrac{1}{2} m\dot{x}^2 + \tfrac{1}{2} k_1 x^2 + \tfrac{1}{6} k_2 x^3 = \bar{h} \tag{2}$$

where $\bar{h}$ is the energy of the system.

Or,

$$\frac{dx}{dt} = (\mathrm{A} - \omega^2 x^2 + 4\alpha x^3)^{\frac{1}{2}} \tag{3}$$

where

$$\mathrm{A} = \frac{2\bar{h}}{m}\,; \qquad \omega^2 = \frac{k_1}{m} \quad \text{and} \quad 4\alpha = -\frac{k_2}{3m}.$$

Before proceeding further, we consider the roots of the expression

$$f(x) = (4\alpha x^3 - \omega^2 x^2 + \mathrm{A}) \tag{4}$$

which define the regions wherein the right-hand side of (3) is real. The discriminant of the cubic, namely $(\mathrm{G}^2 + 4\mathrm{H}^3)$, is equal to

$$64\mathrm{A}\alpha^2\left(4\mathrm{A}\alpha^2 - \frac{\omega^6}{27}\right)$$

and this will be negative as long as

$$\frac{\mathrm{A}\alpha^2}{\omega^6} < \frac{1}{108}. \tag{5}$$

When this condition is satisfied all the three roots of $f(x) = 0$ are real, and two of them will be positive and the remaining one negative. Denoting these roots by x_1, x_2 and x_3 where $x_1 > x_2 > x_3$, we have

$$f(x) = 4\alpha\,(x - x_1)\,(x - x_2)\,(x - x_3). \tag{6}$$

Now $\{f(x)\}^{\frac{1}{2}}$ is real in two cases, *viz.*, (i) when $x > x_1$, or (ii) when x lies in the region $x_2 \geqslant x \geqslant x_3$.

For $x > x_1$,* the force acting on the molecule becomes repulsive and it increases with increasing distance of the oscillator from the origin. The vibrations in this case are unstable and the oscillator flies off to infinity within

---

* The solution in this case is given by $x = x_2 + (x_1 - x_2)\, nc^2\,(u, k)$. Since $cn\,(u, k)$ has zeros at points $u = (2n + 1)\,\mathrm{K}$, where n is an integer, the displacement is infinite at these points. Thus within a period $t = \pi/\tilde{\omega}$ after crossing the point x_1, the molecule dissociates.

a short period after crossing the point x_1. In other words, when the internuclear distance of a diatomic molecule exceeds its equilibrium value by an amount x_1, the molecule will dissociate.

The vibrations in the region $x_2 \geqslant x \geqslant x_3$ are stable and retain in a measure the characteristics of a harmonic oscillator. Writing

$$\tau = \frac{A^{\frac{1}{2}}a}{\omega^3},$$

the roots of $f(x) = 0$ are approximately

$$x_1 = \frac{\omega^2}{4a}(1 - 16\tau^2 - 512\tau^4)$$

$$x_2 = \frac{\sqrt{A}}{\omega}(1 + 2\tau + 10\tau^2 + 64\tau^3 + 224\tau^4)$$

$$x_3 = -\frac{\sqrt{A}}{\omega}(1 - 2\tau + 10\tau^2 - 64\tau^3 + 224\tau^4). \tag{7}$$

The above relations were derived by using the bionomial expansion in the expressions for the roots of the cubic, assuming that τ is small. One can however easily verify by substitution that they satisfy the equation $f(x) = 0$ upto terms of the order of ω^{-9}. Equation (3) can now be written as

$$t = \frac{1}{2\sqrt{a}} \int_{x_3}^{x} \frac{dx}{\{(x - x_1)(x - x_2)(x - x_3)\}^{\frac{1}{2}}}. \tag{8}$$

The right-hand side of the above equation is an elliptic integral and its value[4] is

$$\frac{1}{2\sqrt{a}} \times \frac{2}{\sqrt{x_1 - x_3}} \, sn^{-1}\left(\sqrt{\frac{x - x_3}{x_2 - x_3}}, \sqrt{\frac{x_2 - x_3}{x_1 - x_3}}\right).$$

Hence writing $u = \sqrt{a(x_1 - x_3)}\, t$ and

$$k^2 = \frac{(x_2 - x_3)}{(x_1 - x_3)},$$

we get the wellknown solution

$$x = x_3 + (x_2 - x_3)\, sn^2(u, k). \tag{9}$$

Given the energy of the oscillator, the above equation determines its complete course in time.

In view of their periodicity properties, the Jacobian elliptic functions admit of expansions as Fourier series. For the function $sn^2(u, k)$, we have the following expansion[5] (see Whittaker and Watson, p. 520, example 5):

$$sn^2(u, k) = \left(\frac{\pi}{k\mathrm{K}}\right)^2 \left\{\frac{\mathrm{K}(\mathrm{K}-\mathrm{E})}{\pi^2} - 2\sum_{n=1}^{\infty} \frac{nq^n}{(1-q^{2n})} \cos 2ny\right\} \tag{10}$$

where

$$y = \frac{\pi}{2\mathrm{K}} u; \tag{11}$$

K and E are the complete elliptic integrals of the first and second type which in terms of hyper-geometric functions are defined by

$$\mathrm{K} = \frac{\pi}{2} \mathrm{F}(\tfrac{1}{2}, \tfrac{1}{2}, 1; k^2)$$

$$\mathrm{E} = \frac{\pi}{2} \mathrm{F}(-\tfrac{1}{2}, \tfrac{1}{2}, 1; k^2) \tag{12}$$

and q is a parameter which is related to the modulus k of the elliptic function by means of the formula

$$q = \epsilon + 2\epsilon^5 + 15\epsilon^9 + 150\epsilon^{13} + 0(\epsilon^{17}) \tag{13}$$

where again

$$2\epsilon = \frac{1 - \sqrt{k^1}}{1 + \sqrt{k^1}}$$

and

$$k^1 = (1 - k^2)^{\frac{1}{2}}.$$

Substituting (10) in (9) we get

$$x = x_3 + \frac{(x_2 - x_3)}{(\mathrm{K}k)^2} \left[\mathrm{K}(\mathrm{K}-\mathrm{E}) - 2\pi^2 \sum_{n=1}^{\infty} \frac{nq^n}{(1-q^{2n})} \cos 2ny\right]. \tag{14}$$

Equation (14) shows that the displacement of the oscillator is no longer a simple sinusoidal function, but contains a constant term and harmonics of the fundamental mode. The coefficient of t in $2y$ namely $(\pi/\mathrm{K})\sqrt{\alpha(x_1 - x_3)}$

gives the circular frequency of the system. Denoting this by ϖ, we have therefore

$$\varpi = \frac{\pi}{\mathrm{K}} \sqrt{a(x_1 - x_3)} \tag{15}$$

The shift $\langle x \rangle$ in the mean position of the oscillator is given by the constant term of the expansion (14) and is equal to

$$x_3 + \frac{(x_2 - x_3)(\mathrm{K} - \mathrm{E})}{\mathrm{K}k^2} \tag{16}$$

The amplitude of the nth harmonic is proportional to

$$\frac{nq^n}{(1 - q^{2n})}. \tag{17}$$

In particular the intensities of the first three harmonics are in the ratio

$$\frac{q^2}{(1-q^2)^2} : \frac{4q^4}{(1-q^4)^2} : \frac{9q^6}{(1-q^6)^2}. \tag{17a}$$

Equations (15) and (16) express the frequency of the oscillator and its mean shift as functions involving elliptic integrals. We shall now obtain approximations for these which are useful for appreciating their physical magnitudes as well as for comparison with earlier work.

The following expansions now hold good for k^2, K, $(\mathrm{K} - \mathrm{E})$ and $\sqrt{a(x_1 - x_3)}$ when $\tau \ll 1$:

$$\begin{aligned} k^2 &= 8\tau(1 - 4\tau + 50\tau^2 - 336\tau^3 + 3694\tau^4) \\ \mathrm{K} &= \frac{\pi}{2}(1 + 2\tau + \tau^2 + 78\tau^3) \\ \sqrt{a(x_1 - x_3)} &= \frac{\omega}{2}(1 + 2\tau - 14\tau^2 + 48\tau^3) \\ (\mathrm{K} - \mathrm{E}) &= 2\pi\tau(1 - \tau + 41\tau^2 - 80{\cdot}5\tau^3). \end{aligned} \tag{18}$$

Substituting (7) and (18) in (15) and (16), one finds after some simplification that the change in frequency of the oscillator and its mean displacement from the origin are approximately given by

$$(\varpi - \omega) = \frac{-15\mathrm{A}a^2}{\omega^5} \tag{19}$$

$$\langle x \rangle = \frac{3\mathrm{A}a}{\omega^4} + \frac{225}{2}\frac{\mathrm{A}^2a^3}{\omega^{10}} \tag{20}$$

respectively. The reader can easily see these to be the same as the expressions given in books on acoustics.

3. SOME REMARKS

We shall now consider how the frequency and mean shift of the oscillator get modified when the energy of the system is altered. Remembering that the quantity A occurring in equations (19, 20) is a constant multiple $(2/m)$ of the energy $\bar{h}$ of the system, we get on differentiation of (19) with respect to $\bar{h}$ that

$$\frac{d\tilde{\nu}}{d\bar{h}} = \frac{-15a^2}{\pi m\omega^5} \tag{21}$$

where

$$\tilde{\nu} = \frac{\tilde{\omega}}{2\pi}.$$

Thus to an approximation which ignores terms of the order of τ^4, we see that the frequency of the oscillator is a decreasing function of the energy, the rate of decrease being a constant characteristic of the oscillator.

From (21) it follows that the change in the frequency of the system as its energy is increased from ϵ_1 to ϵ_2 is

$$\frac{-15a^2}{\pi m\omega^5}(\epsilon_2 - \epsilon_1).$$

Writing $\epsilon_2 = (v + 3/2)\,h\nu$ and $\epsilon_1 = (v + \frac{1}{2})\,h\nu$, we see that this is equal to

$$\frac{-15a^2}{\pi m\omega^5}\,h\nu$$

or

$$\frac{-5}{48}\,\frac{k_2{}^2 h\nu}{\pi (mk_1{}^5)^{\frac{1}{2}}}$$

which is the value given by the perturbation theory.[6] Hence in this case even a semi-classical theory is able to give the correct results yielded by wave-mechanics.

Differentiating now (20) with respect to $\bar{h}$, one finds that

$$\frac{d\langle x\rangle}{d\bar{h}} = \frac{6a}{m\omega^4} + \frac{900a^3}{(m\omega^5)^2}\,\bar{h} \tag{22}$$

which shows that the mean shift of the oscillator increases with rise in the energy of the system.

As before, the magnitude of the shift in the vth state may be obtained by writing $\epsilon_v = (v + \frac{1}{2})\, h\nu$ in (20). We have

$$\langle x \rangle_v = \frac{3ah}{\pi m\omega^3}(v + \tfrac{1}{2}) + \frac{225}{2}\frac{h^2a^3}{\pi^2m^2\omega^8}(v + \tfrac{1}{2})^2. \tag{23}$$

From the above, it is possible to obtain the stretch (or contraction) in the bond-length of a diatomic molecule during a transition between two different quantum states specified by the numbers v and v' respectively. This is given by

$$\frac{3ah}{\pi m\omega^3}(v' - v) + \frac{225}{2}\frac{h^2a^3}{\pi^2m^2\omega^8}(v' - v)(v' + v + 1) \tag{24}$$

4. The Energy Levels

The Schrodinger equation for the oscillator is given by

$$\frac{d^2u}{dx^2} + \frac{8\pi^2m}{h^2}(\epsilon - \mathrm{V})\, u = 0 \tag{25}$$

where V has the form given in (1). A method for determining the eigenvalues of an equation of the above type was developed by Wentzel, Kramers and Brillouin, and this was later refined by Langer.[7] According to the latter, if x_3 and x_2 are two consecutive simple zeroes of $\epsilon - \mathrm{V}(x)$ such that $\epsilon > \mathrm{V}$ for $x > x_3$, and $\epsilon < \mathrm{V}$ for $x > x_2$, the eigenvalues of (25) are determined by

$$(n + \tfrac{1}{2})\pi = \int_{x_3}^{x_2} \left\{\frac{8\pi^2m}{h^2}(\epsilon - \mathrm{V})\right\}^{\frac{1}{2}} dx. \tag{26}$$

Writing $\mathrm{A} = 2\epsilon/m$, the above equation becomes

$$(n + \tfrac{1}{2})\pi = \frac{2\pi m}{h}\,\mathrm{I} \tag{27}$$

where

$$\mathrm{I} = \int_{x_3}^{x_2} (4ax^3 - \omega^2x^2 + \mathrm{A})^{\frac{1}{2}}\, dx.$$

The integral I has been evaluated in Appendix I and substituting the value given for it there in (27), one gets

$$(n + \tfrac{1}{2})\, h = \frac{8m}{15}\sqrt{a\eta_2}\,\{-(\mathrm{K} - \mathrm{E})\,[\Sigma(x_2 - x_3)^2] + \eta_1(\eta_1 + \eta_2)\,\mathrm{K}\} \tag{28}$$

where $\eta_1 = (x_2 - x_3)$ and $\eta_2 = (x_1 - x_3)$.

The quantities occurring on the right-hand side of the above equation are all functions of ϵ and hence by solving this transcendental equation for different integral values of n, the eigenvalues $\epsilon_1, \epsilon_2, \ldots\ldots\ldots \epsilon_n$ of the oscillator may be determined.

In practice, equation (28) can be solved by expressing the right-hand side as a power series in the parameter τ which will result in a series expansion in ϵ and then inverting the series. For example, by making use of the expansions (7) and (18) and further of the following relations

$$\Sigma (x_2 - x_3)^2 = \frac{\omega^4}{8a^2}\,; \tag{29}$$

$$\eta_1 (\eta_1 + \eta_2) = \frac{\sqrt{A}\omega}{2a} (1 + 12\tau - 14\tau^2 + 240\tau^3)$$

it can be seen that (28) is equivalent to

$$(n + \tfrac{1}{2})\, h = 2m \cdot \frac{\pi A}{2\omega} \left(1 + \frac{15}{2}\, \tau^2 + 0\,(\tau^4)\right). \tag{30}$$

Or, writing $a = -k_2/12m$, $\omega = 2\pi\nu$ and $A = 2\epsilon/m$ we have

$$(n + \tfrac{1}{2})\, h\nu = \epsilon + \frac{5}{96\pi\nu} \frac{k_2^2}{(mk_1^5)^{\frac{1}{2}}}\, \epsilon^2.$$

Hence

$$\epsilon = (n + \tfrac{1}{2})\, h\nu - \frac{5}{96} \frac{k_2^2 h^2 \nu}{\pi\, (mk_1^5)^{\frac{1}{2}}} (n + \tfrac{1}{2})^2 \tag{31}$$

which is the eigenvalue of the oscillator as obtained from the perturbation theory correct to the second order. By expanding (25) still further than in (27), one can obtain higher order corrections.

The author's grateful thanks are due to Professor Sir C. V. Raman for his kind interest in this work.

SUMMARY

Exact expressions have been obtained for the frequency of an anharmonic oscillator, the shift in its equilibrium position from the origin and for the amplitudes of its different harmonics. It is shown that the frequency of the oscillator is a decreasing function of the energy and that some of the results of wave-mechanics can be obtained from the classical theory by substituting in the classical energy of the oscillator the different energy values of a harmonic oscillator. The eigenvalues of the oscillator are determined by using the W.K.B. method. The classical theory of a Morse oscillator has similarly been worked out in Appendix II.

References

1. Lord Rayleigh .. *Theory of Sound*, 1948, pp. 76–78.
2. Herzberg, G. .. *Spectra of Diatomic Molecules*, Second Edition, pp. 90–102.
3. Fermi, E. .. *Moleküle und Kristalle*, p. 140.
4. Magnus, W. and Oberhettinger *Formulas and Theorems for the Special Functions of Mathematical Physics*, 1949, 108.
5. Whittaker and Watson .. *Modern Analysis*, Fourth Edition (Chapters XXI and XXII).
6. Ta-You-Wu .. *Vibrational Spectra and Structure of Polyatomic Molecules*, 1939, 48.
7. Langer, R. E. .. *Phys. Rev.*, 1937, **51**, 669.
8. Morse, P. M. .. *Ibid.*, 1929, **34**, 57.

APPENDIX 1

Evaluation of the integral $\mathrm{I} = \int_{x_3}^{x_2} \sqrt{4ax^3 - \omega^2 x^2 + \mathrm{A}}\, dx.$

Obviously we have

$$\mathrm{I} = \int_{x_3}^{x_2} \frac{(4ax^3 - \omega^2 x^2 + \mathrm{A})}{2\sqrt{a}\,\{(x - x_1)(x - x_2)(x - x_3)\}^{\frac{1}{2}}}\, dx. \tag{1}$$

If we substitute $(x - x_3) = y^2$ in the above equation and denote by Q_m the integral

$$\int_0^{\sqrt{\eta_1}} \frac{x^m dx}{\sqrt{(x^2 - \eta_1)\,(x^2 - \eta_2)}}$$

where $\eta_1 = (x_2 - x_3)$ and $\eta_2 = (x_1 - x_3)$, equation (1) takes the form

$$\mathrm{I} = (p\mathrm{Q}_6 + q\mathrm{Q}_4 + r\mathrm{Q}_2 + s\mathrm{Q}_0) \tag{2}$$

where

$$p = 4\sqrt{a}\,;$$

$$q = \sqrt{a}\left(12x_3 - \frac{\omega^2}{a}\right);$$

$$r = \sqrt{a}\left(12x_3^2 - \frac{2\omega^2 x_3}{a}\right); \quad \text{and}$$

$$s = \frac{1}{\sqrt{a}}(4ax_3^3 - \omega^2 x_3^2 + \mathrm{A}).$$

Since x_3 is a root of $f(x) = 0$, the constant s in the above is equal to zero.

The integrals Q_m can be evaluated by reduction formulæ. For example,

$$\frac{d}{dx}\{x^3\sqrt{\mathrm{Q}}\} = \frac{3x^2\mathrm{Q}}{\sqrt{\mathrm{Q}}} + \frac{x^3\mathrm{Q}'}{2\sqrt{\mathrm{Q}}}$$

where

$$\mathrm{Q} = \sqrt{(x^2 - \eta_1)\,(x^2 - \eta_2)}.$$

If we integrate this equation between 0 and $\eta_1^{\frac{1}{2}}$, the left-hand side vanishes and we get

$$\mathrm{Q}_6 = \frac{1}{5}(4a\mathrm{Q}_4 - 3b\mathrm{Q}_2) \tag{3}$$

where

$$a = (\eta_1 + \eta_2) \qquad \text{and} \qquad b = \eta_1\eta_2.$$

Similarly

$$Q_4 = \tfrac{1}{3}(2aQ_2 - bQ_0). \tag{4}$$

Substituting (3) and (4) in (2) we get after some reduction that

$$I = -\frac{4}{15}\sqrt{a}\{2Q_2(x_1^2 + x_2^2 + x_3^2) - abQ_0\}. \tag{5}$$

Now

$$Q_0 = \int_0^{\sqrt{\eta_1}} \frac{dx}{\sqrt{Q}} = \frac{K}{\sqrt{\eta_2}}. \tag{6}$$

Next by the substitution $x = z\sqrt{\eta_1}$, we find that

$$Q_2 = \frac{\eta_1}{\sqrt{\eta_2}} \int_0^1 \frac{z^2 dz}{\{(1 - z^2)(1 - k^2z^2)\}^{\frac{1}{2}}}$$

where

$$k^2 = \frac{\eta_1}{\eta_2}$$

$$\text{Or } Q_2 = \frac{\eta_1}{\sqrt{\eta_2}} \int_0^K sn^2(u, k)\, du = \sqrt{\eta_2}(K - E). \tag{7}$$

Substituting (6) and (7) in (5), one gets

$$I = \frac{4}{15}\sqrt{a\eta_2}\{-\Sigma(x_2 - x_3)^2(K - E) + \eta_1(\eta_1 + \eta_2)K\} \tag{8}$$

APPENDIX II

The potential (1, Section 2) is valid, when the vibrations are small but nevertheless depart from harmonicity. Apart from its applications in acoustics, it is useful in studying anharmonicity in complex molecules when one splits their vibrations into those of an assembly of anharmonic oscillators. For diatomic molecules however Morse[8] suggested a potential given by

$$V = D(1 - e^{-\beta x})^2 \tag{1}$$

where D is the dissociation energy of the molecule and β is a constant, which holds good approximately upto the dissociation range. The quantum mechanical energy values of an oscillator moving in a potential field of the type (1) was given by Morse. We give below the classical theory of such an oscillator which merits attention in view of its extreme simplicity and for purposes of comparison with the quantum theory.

The equation of energy for the Morse oscillator is

$$\tfrac{1}{2} m\dot{x}^2 + D(1 - e^{-\beta x})^2 = \bar{h} \tag{2}$$

where as before $\bar{h}$ denotes the energy of the system. Hence

$$\dot{x}^2 = c + by + ay^2 \tag{3}$$

where

$$c = \frac{2}{m}(\bar{h} - D); \quad b = \frac{4D}{m}; \quad a = \frac{-2D}{m}$$

and

$$y = e^{-\beta x}. \tag{4}$$

c can immediately be seen to be negative.

The turning points for the oscillator in its course are $-1/\beta \log (1 + \sqrt{h/D})$ and $-1/\beta \log. (1 - \sqrt{h/D})$. We shall measure time from the instant the oscillator is at its extremity in the left.

From (3) and (4) we get

$$t = -\frac{1}{\beta} \int \frac{dy}{y\sqrt{ay^2 + by + c}} \tag{5}$$

or

$$\beta t = \frac{1}{\sqrt{-c}} \cos^{-1} \frac{by + 2c}{y\sqrt{b^2 - 4ac}}. \tag{6}$$

Hence we have

$$x = \frac{1}{\beta}\log\frac{D}{(D-\bar{h})} + \frac{1}{\beta}\log\left\{1 - \sqrt{\frac{\bar{h}}{D}}\cos\beta t\sqrt{\frac{2}{m}(D-\bar{h})}\right\} \quad (7)$$

The above equation determines the course of the oscillator with time.

From (7) it is immediately obvious that the frequency of the gravest mode is given by

$$\tilde{\nu} = \frac{\beta}{2\pi}\sqrt{\frac{2}{m}(D-\bar{h})} \quad (8\,a)$$

$$= \nu\left(1 - \frac{\bar{h}}{D}\right)^{\frac{1}{2}} \quad (8\,b)$$

where

$$\nu = \frac{\beta}{2\pi}\sqrt{\frac{2D}{m}};$$

ν will be the (harmonic oscillator) frequency of the system when the anharmonic terms in the expansion of (1) as a power series in x are neglected.

The eigenvalues of a Morse oscillator are

$$E_n = (n+\tfrac{1}{2})h\nu - z(n+\tfrac{1}{2})^2 h\nu \quad (9)$$

where

$$z = \frac{\beta^2 h}{8\pi^2 m\nu} = \frac{h\nu}{4D}. \quad (10)$$

The frequency of emission of the oscillator during a transition from the nth state to the one immediately below it is given by

$$\nu_{n,n-1} = \nu_n{}^{em} = \nu(1-2nz)$$

$$= \nu\left\{z + \sqrt{1 - \frac{4zE_n}{h\nu}}\right\}$$

$$= \nu\left\{z + \sqrt{1 - \frac{E_n}{D}}\right\} \quad (11\,a)$$

from (10).

Similarly the frequency of absorption from the nth state is given by

$$\nu_n{}^{ab} = \nu_{n+1,n} = \nu\left\{-z + \sqrt{1 - \frac{E_n}{D}}\right\}. \quad (11\,b)$$

Equation (8 *b*) shows that the frequency of the classical oscillator is a decreasing function of its energy. The dependence of the frequencies of

emission or absorption on the transitional energy levels is likewise described by (11 *a*) and (11 *b*). Apart from the first term which is a consequence of the quantum phenonmenon that has no classical analogue, namely, that the molecule possesses a zero-point energy and on the non-linear dependence of the energy levels on the quantum numbers, the formulæ (11) possess a striking resemblance to the classical formula (8 *b*). In fact $(\nu_n{}^{ab} + \nu_n{}^{em})/2$ depends on the energy of the nth level in the same way as the classical frequency does with the energy of the system. When the energy equals its dissociation value the discrete spectrum stops for the oscillator.[8] Classically its frequency then vanishes.

In order to find out the shift in the mean position of the oscillator and the amplitudes of the different harmonics, we express x as a Fourier cosine series in the form

$$x = a_0 + \sum_{n=1}^{\infty} a_n \cos nu \tag{12}$$

where $u = 2\pi\,\tilde{\nu}t$. Then

$$\begin{aligned} a_0 &= \frac{1}{\beta}\log\frac{D}{(D-h)} + \frac{1}{2\pi\beta}\int_{-\pi}^{+\pi}\log\left(1-\sqrt{\frac{h}{D}}\cos u\right)du \\ &= \frac{1}{\beta}\log\frac{D}{(D-h)} + \frac{1}{\beta}\log\tfrac{1}{2}\left\{1+\sqrt{1-\frac{h}{D}}\right\} \\ &= \frac{1}{\beta}\log\tfrac{1}{2}\left\{\frac{1+\sqrt{1-\frac{h}{D}}}{1-\frac{h}{D}}\right\}. \end{aligned} \tag{13}$$

From the above it follows that the shift in the mean position of the oscillator increases with the energy of the system and tends logarithmically to infinity when the energy approaches its dissociation value.

Next we have

$$a_n = \frac{1}{\pi\beta}\int_{-\pi}^{\pi}\log\left(1-\sqrt{\frac{h}{D}}\cos u\right)\cos mu\,du. \tag{14}$$

The integral may be evaluated by expanding the logarithmic function as a power series, and integrating term by term the resulting series which can be seen to be uniformly convergent for all values of u in $(-\pi, \pi)$. Thus one gets

$$a_n = -\frac{1}{\beta} \sum_{s=n/2}^{\infty} \left(\frac{\bar{h}}{\mathrm{D}}\right)^s \frac{1}{2s2^{2s-1}} \binom{2s}{\frac{2s-n}{2}} \tag{15 a}$$

for even values of n and

$$a_n = -\frac{1}{\beta} \sum_{s=n-1/2}^{\infty} \left(\frac{\bar{h}}{\mathrm{D}}\right)^{2s+1/2} \frac{1}{(2s+1)\,2^{2s}} \binom{2s+1}{\frac{2s+1-n}{2}} \tag{15 b}$$

for odd values of n.

The above formulæ give the law of dependence of the amplitudes of the various harmonics on the energy of the oscillator. One notices that the amplitude of the nth harmonic is of the order of $(\bar{h}/\mathrm{D})^{n/2}$.

STABILITY OF METAL-CHELATE COMPOUNDS OF BENZOPYRONE DERIVATIVES

By G. M. Saxena and T. R. Seshadri, F.A.Sc.

(Department of Chemistry, University of Delhi, Delhi)

Received May 20, 1957

The benzo-γ-pyrone derivatives—chromones, flavones, isoflavones and xanthones—constitute a group of closely related compounds that occur extensively in nature. In each of these sub-groups, chemical evidence based on low acid-dissociation and difficulty of methylation of the hydroxyl group and ferric chloride reaction, indicates the existence of hydrogen bonds between the carbonyl group and the hydroxyl group in the 5- and 3-positions of the chromone ring. Following the procedure suggested by Bate-Smith and Westall,[1] Simpson and Garden[2] have found by chromatography that chelation with the 5-hydroxyl group is much stronger than that with the 3-hydroxyl group. But no quantitative information is available regarding the variations in the stabilities of this bond depending on structural features of the different groups of compounds.

No systematic work seems to have been done for the utilisation of benzopyrone derivatives in analytical chemistry. The formation of an ether-soluble highly fluorescent complex with boric acid and citric acid has been considered specific for flavonols[3] and the formation of zirconium complexes with flavones and flavonols has been recorded by Horhammer [4, 5] and the reactions of flavonoids with copper, cadmium and titanium[6] and heavy metals[7] have also been described. However, only two compounds have so far been put to actual analytical use. Morin has been employed for the detection of aluminium,[8] tin,[9] titanium and zirconium[10] and for the determination of tin,[11] thorium[12] and uranium.[13] Quercetin has been used for the detection of iron and uranium[14] and for the determination of germanium[15] and zirconium.[16]

As a preliminary to a systematic study of the analytical uses of benzopyrone derivatives, a comparison of the stability of metal chelates formed by typical members has been undertaken. To avoid complications, only monohydroxy compounds have been chosen and the free hydroxyl group is left in the 5- or the 3-position of flavones and chromones, 5-position of isoflavones and diphenyl chromones and 1-position of xanthones. In certain cases methoxyl groups are introduced in the 7-position (3-position in xanthone) since this position is invariably substituted in natural flavonoids and such

substituted compounds are also easier to prepare; it may be significant to note that the 5-hydroxyl group which is the most active in chelation is most difficult to methylate and 5-hydroxy-7-methoxy compounds of flavonoids are readily made by partial methylation of 5: 7-dihydroxy derivatives. The list of compounds examined is given in Table I arranged according to the strength of the metal chelate bond.

For the determination of the degree of formation of the complex (n) the method of Calvin and Wilson[17] has been adopted. Copper ions have been used as the standard and the formation constants of this metal ion with each of the benzopyrone derivatives as ligand have been determined in aqueous dioxan medium (2 vol. water: 1 vol. dioxan) potentiometrically. These authors have shown that this titration can be done without entailing serious error using a glass electrode over the whole pH range. In view of the limited objective of our experiments minor interferences have not been taken into account. M/100 Solutions of the ligands in dioxan have been titrated in the presence of excess of aqueous perchloric acid with normal alkali solution both in the presence and absence of cupric ions. Since preliminary experiments showed that there was no chelation in the presence of sulphate ions (see also Burkin[17a]), copper nitrate solution has been employed. For the determination of stability constants the method of Irving and Rossotti[18] has been employed. Since the values of $\bar{n}$, the degree of formation, are considerably below 1·5 in each case, only the value of K_1 could be determined. It would appear, therefore, that the higher complex CuL_2 has little stability. The values of log K_1 are given in Table I.

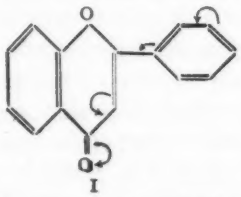
TABLE I

		log K_1	pK_a
1.	1-Hydroxy-3-methoxy xanthone	4·80	10·72
2.	1-Hydroxy xanthone ..	4·70	10·72
3.	5-Hydroxy-7-methoxy flavone ..	3·45	8·10
4.	5-Hydroxy flavone ..	3·40	8·10
5.	3-Hydroxy-7-methoxy flavone ..	3·01	7·90
6.	3-Hydroxy flavone ..	3·00	7·90
7.	2-Methyl-5-hydroxy-7-methoxy chromone ..	2·57	7·85
8.	2-Methyl-5-hydroxy chromone ..	2·50	7·90
9.	2-Methyl-3-hydroxy-7-methoxy chromone ..	2·30	7·86
10.	2: 3-Diphenyl-5-hydroxy-7-methoxy chromone ..	2·10	8·05
11.	5-Hydroxy-7-methoxy isoflavone ..	2·00	8·10

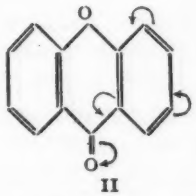
The results show that the metal-chelate ring in xanthone is the strongest. Next in order of stability are the 5-hydroxy flavones followed by 3-hydroxy

flavones. In metal-chelation, isoflavones are weaker than even the chromones and 2:3-diphenyl chromones come in between them. Obviously, the position of the phenyl group plays an important part. The 2-position is highly favourable (*cf.* flavones and chromones). It should also be pointed out that the presence of a methoxyl group in the 3-position in xanthones or the 7-position in chromones, flavones and isoflavones exerts a favourable influence, though not very marked.

The observations seem to be in agreement with expectations based on the structure of chelate bonds and the influence of substituents on them. The two participants in the chelate bond are (*a*) the carbonyl donor group, C = O and (*b*) the hydrogen atom of the hydroxyl group (or the metal ion). The electron-availability at the donor oxygen atom is increased by a phenyl group present in conjugation with the carbonyl group in flavones (I) and the bond formed is thus much stronger than it is in chromones. In a similar manner, the fused benzene ring in xanthone also augments electron-availability at the carbonyl group (II).



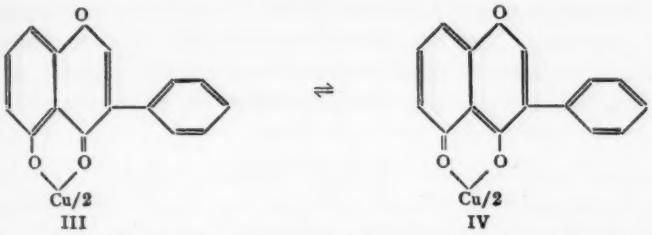
I



II

The difference in the stability of the five-membered and six-membered chelate rings is evident from the stability constants of 5-hydroxy- and 3-hydroxy-flavones and chromones.

The abnormally low values of K_1 obtained for isoflavone complexes require explanation. In isoflavones, the phenyl group is not in conjugation with the carbonyl group and hence electron-availability should be the same as for the corresponding chromone. However, as was pointed out by Calvin and Wilson,[17] the stability of metal-chelate bond is governed by two factors: (1) electron-availability and (ii) resonance of the type indicated by formulæ (III) and (IV). The presence of phenyl group in the 3-position hinders the resonance. As a matter of fact, in molecular models it could be seen that the 3-phenyl group makes it difficult to produce planar copper complex (IV). It may be pointed out, however, that this weakening of the chelate ring in isoflavones is operative only in metal-chelate formation and not in hydrogen bond formation. This can readily be seen from the pK_a values of 2-methyl-5-hydroxy-7-methoxy chromone and 5-hydroxy-7-methoxy isoflavone, being 7·85 and 8·1 respectively.



From the above reasoning it will be clear that in 2: 3-diphenyl chromones two opposing factors play their part. As a consequence these compounds have a slightly higher log K_1 value than the simpler isoflavones.

The effect of methoxyl substituent in the 3-position in xanthones and in the 7-position of chromones becomes explicable since it will increase electron-availability at the carbonyl group by electromeric effect and thus facilitate chelation.

Preparation of the reagents:

2-*Methyl*-5-*hydroxy chromone* and 5-*hydroxy flavone* have been prepared from γ-resacetophenone by heating with sodium acetate and acetic anhydride in the case of the former[19] and sodium benzoate and benzoic anhydride in the case of the latter.[20] Employing phloracetophenone in a similar manner and effecting partial methylation, 2-*methyl*-5-*hydroxy*-7-*methoxy chromone*[21] and 5-*hydroxy*-7-*methoxyflavone* have been obtained.[22] Allan-Robinson condensation of 2: 4: 6-trihydroxy-phenyl-benzyl ketone with sodium benzoate and benzoic anhydride yielded 2: 3-diphenyl-5: 7-dihydroxy-chromone.[23] It is more convenient to use for this preparation Baker-Venkataraman reaction recently reported by Gupta and Seshadri.[24] Subsequent partial methylation with dimethyl sulphate (1·1 mole) and dry potassium carbonate in dry acetone solution yielded the 7-methyl ether.

5-*Hydroxy*-7-*methoxyisoflavone* has been made by the ethyl formate method using 2-hydroxy-4: 6-dimethoxy-phenyl-benzyl ketone and subsequent partial demethylation of the dimethyl ether with hydriodic acid using mild conditions.[25]

The most convenient procedure for preparing 3-*hydroxy*-7-*methoxy flavone* is the partial demethylation of 3: 7-dimethoxy flavone using aluminium chloride and nitrobenzene.[26] A similar method has been used for the preparation of 2-methyl-3-hydroxy-7-methoxy chromone. The substance crystallised from methanol as colourless rectangular prisms, m.p. 220–21° (decomp.) (Found: C, 64·4, H, 4·4; $C_{11}H_{10}O_4$ requires C, 64·1; H, 4·9%).

For the preparation of 3-*hydroxy flavone* the method of nuclear reduction has been employed. For this purpose, 3-methoxy-7-hydroxy flavone[27] was tosylated and subjected to reduction in the presence of Raney nickel.[28] The product was 3-methoxy flavone, which was then demethylated with hydriodic acid.[28]

1-*Hydroxy xanthone and* 1-*hydroxy*-3-*methoxy xanthone* have been prepared by condensation of salicylic acid with resorcinol[29] and phloroglucinol dimethyl ether[30] respectively in the presence of fused zinc chloride.

SUMMARY

A comparative study of hydroxy-benzopyrone derivatives has been made with reference to their capacity to form chelate combinations with metals. Based on the determination of stability constants it could be concluded that 1-hydroxy xanthone forms the most stable complex. Addition of a methoxyl group in the 3-position has a favourable influence. Among the flavones a hydroxyl group in the 5-position forms definitely a stronger complex as compared with the 3-hydroxyl group. Here also addition of a methoxyl group in the 7-position is an advantage. Similar results are obtained with the chromones though their complexes are comparatively weaker. Isoflavone derivatives unexpectedly form the weakest complexes and in this case steric factors seem to be involved. The presence of this factor could be noticed in the case of 2:3-diphenyl chromones also which also have abnormally weak complexes.

REFERENCES

1. Bate-Smith and Westall .. *Biochem. Biophys. Acta*, 1950, **4**, 427.
2. Simpson and Garden .. *J.C.S.*, 1952, 4638.
3. Wilson .. *J. Amer. Chem. Soc.*, 1939, **61**, 2303.
   Tauböck .. *Naturwiss.*, 1942, **30**, 439.
4. Hörhammer and Hansel .. *Arch. der Pharm.*, 1951, **284**, 276.
5. Hörhammer .. *Naturwiss.*, 1954, **41**, 529.
6. Neu and Hagedorn .. *Z. anal. Chim.*, 1953, **139**, 96; *Naturwiss.*, 1953, **40**, 411.
7. Brune .. *Naturwiss*, 1954, **41**, 373.
8. Goppelsroeder .. *Z. anal. Chem.*, 1868, **7**, 195.
   Eagriwe .. *Ibid.*, 1929, **76**, 440.
9. Feigl and Gentil .. *Mikrochim. Acta*, 1954, 90.
10. Almassy .. *Science*, 1954, **119**, 74, 76, 77.
11. Patrovsky .. *Chem. Listy*, 1953, **47**, 676.
12. Beck and Hantos .. *Magyar Kem. Folyoirat*, 1954, **60**, 244;
    Fletcher and Milkey .. *Science*, 1954, **119**, 445.

13. Tomic and Hecht .. *Mikrochim. Acta*, 1955, 896.
14. Kocsis .. *Mikrochemie*, 1938, **25**, 13.
15. Oka and Matsuo .. *J.C.S.*, Japan, 1953, **74**, 931.
16. Grimaldi and White .. *Anal. Chem.*, 1953, **25**, 1886.
17. Calvin and Wilson .. *J. Amer. Chem. Soc.*, 1945, **67**, 2003.
17*a*. Burkin .. *Quart. Rev.*, 1951, **5**, 1.
18. Irving and Rossotti .. *J.C.S.*, 1953, 3397.
19. Limaye and Kelkar .. *Rasayanam*, 1936, 24.
20. Rao, Rajagopalan and Seshadri *Proc. Ind. Acad. Sci.*, 1947, **25 A**, 436.
21. Murti and Seshadri .. *Ibid.*, 1949, **30 A**, 107.
Seshadri *et al.* .. *Ibid.*, 1953, **37 A**, 127.
22. Robinson and Venkataraman *J.C.S.*, 1926, 2347.
Rao, Rao and Seshadri .. *Proc. Ind. Acad. Sci.*, 1947, **25 A**, 428.
23. Baker and Eastwood .. *J.C.S.*, 1929, 2897.
24. Gupta and Seshadri .. *J.S.I.R.*, 1957, **16 B**, 116.
25. Aghoramurthy *et al.* .. *Proc. Ind. Acad. Sci.*, 1951, **33 A**, 57.
26. Krishnaswamy and Seshadri *Ibid.*, 1942, **15 A**, 437.
27. Allan and Robinson .. *J.C.S.*, 1924, **125**, 2192.
28. Gupta, Jain and Seshadri .. *Proc. Ind. Acad. Sci.*, 1953, **38 A**, 470.
29. Pankajamani and Seshadri .. *J.S.I.R.*, 1954, **13 B**, 396.
30. Mittal and Seshadri .. *Ibid.*, 1955, **14 B**, 76.

ROTATIONAL FLOW OF A LIQUID PAST A REGULAR POLYGONAL CYLINDER

By L. V. K. Viswanadha Sarma
(*Indian Institute of Technology, Kharagpur*)

Received December 4, 1956
(Communicated by Dr. B. R. Seth, F.A.SC.)

1. Introduction

The problem of rotational flow of a liquid past cylinders has been considered by many writers. A. R. Mitchell[1] has investigated in detail the flow past circular, elliptic and parabolic cylinders. By an extension of Blasius' theorem for rotational flow, De[3] calculated the thrust due to the flow past cylinders whose cross-sections are bounded by certain family of curves.

In this paper we have considered the rotational flow past a cylinder of regular polygonal cross-section. The problem is simplified by transforming the area outside the polygon into the interior of a unit circle. We have also calculated the thrust on the cylinder due to liquid motion and it is found that the thrust is independent of the number of sides of the polygon provided the length of a side is taken as in (3.4). Further, the case of hypotrochoidal cylinders is considered and the thrust is calculated in each case. It may be noted that though the hypotrochoids belong to the same family of curves considered by De, these curves were excluded from his investigation, and his transformation also was different.

2. Let the undisturbed motion of the fluid consist of uniform velocity $-U$ along the x-axis and uniform vorticity $-\omega$, so that the stream function ψ_2 of the undisturbed flow is given by

$$\psi_2 = Uy - \tfrac{1}{2}\omega y^2.$$

The stream function ψ_1 for the disturbed flow satisfies the equation

$$\nabla^2\psi_1 + \omega = 0.$$

Putting $\psi = \psi_1 - \psi_2$, we have

$$\nabla^2\psi = 0.$$

The boundary conditions are that $\psi \to 0$ at infinity and

$$\psi = -Uy + \tfrac{1}{2}\omega y^2,$$

over the boundary.

3. *Conformal transformation.*—Taking the centre of the polygon as origin in the z-plane, the area outside the polygon can be transformed into the interior of a unit circle in the t-plane by means of the relation[2]

$$\frac{dz}{dt} = \mathrm{A}\frac{\prod_{r=1}^{n}(t - t_r)^{2/n}}{t^2}, \tag{3.1}$$

where $t_1, t_2, \ldots . t_n$ correspond to the n vertices of the polygon and lie on the circle $|t| = 1$. The symmetry of the figure shows that we can take the t's to be the n roots of $t^n = 1$. Thus (3.1) takes the simple form

$$\frac{dz}{dt} = \mathrm{A}\frac{(1 - t^n)^{2/n}}{t^2}. \tag{3.2}$$

By adjusting the constant A, we can write

$$z = \frac{1}{t}(1 - t^n)^{2/n} + 2\int_0^t t^{n-2}(1 - t^n)^{2/n-1}\,dt$$

$$= \frac{1}{t} + \sum_{r=1}^{\infty} a_{rn-1}t^{rn-1}, \tag{3.3}$$

where

$$a_{n-1} = \frac{2}{n(n-1)},$$

$$a_{rn-1} = \frac{2}{n}\left(1 - \frac{2}{n}\right)\left(2 - \frac{2}{n}\right)\ldots\left(r - 1 - \frac{2}{n}\right)\frac{1}{\lfloor r\,(rn-1)}.$$

The infinite series on the right of (3.3) is absolutely convergent for $|t| \leqslant 1$.

The radius of the circumscribed circle is given by

$$d = 1 + \sum_{r=1}^{\infty} a_{rn-1}, \tag{3.4}$$

and a side of the polygon is

$$2d\sin\frac{\pi}{n}.$$

4. On the boundary the stream function ψ satisfies the equation

$$\psi = -\mathrm{U}y + \tfrac{1}{2}\omega y^2 + c$$

$$= -\frac{\mathrm{U}}{2i}(z - \bar{z}) - \tfrac{1}{8}\omega(z - \bar{z})^2 + c, \tag{4.1}$$

where $\bar{z}$ is the complex conjugate of z.

From (3.2)

$$z = \sum_{r=0}^{\infty} a_{rn-1} t^{rn-1} \qquad (a_{-1} = 1),$$

$$(z - \bar{z})^2 = \left(\frac{1}{t} - \frac{1}{\bar{t}}\right)^2 + \sum_{r=1}^{\infty} a^2_{rn-1} (t^{2rn-2} + \bar{t}^{2rn-2} - 2)$$

$$+ \sum_{r=0}^{\infty} \sum_{s=0}^{\infty} a_{rn-1} a_{sn-1} \{t^{rn+sn-2} + \bar{t}^{rn+sn-2}$$

$$- (t^{rn-sn} + \bar{t}^{rn-sn})\}, \quad r \neq s, \tag{4.2}$$

where t is the complex conjugate of t.

Now

$$\sum_{r=0}^{\infty} \sum_{s=0}^{\infty} a_{rn-1} a_{sn-1} t^{rn-sn} = \sum_{m=1}^{\infty} \mathrm{K}_m (t^{nm} + t^{-nm}), \tag{4.3}$$

where

$$\mathrm{K}_m = \sum_{r=0}^{\infty} a_{rn-1} a_{rn+mn-1}. \tag{4.4}$$

Substituting in (4.1) we get

$$\psi = -\frac{\mathrm{U}}{2i}\left[\left(t - \frac{1}{t}\right) + \sum_{r=1}^{\infty} a_{rn-1} (t^{rn-1} - \bar{t}^{rn-1})\right]$$

$$- \tfrac{1}{8}\omega \left[\left(\frac{1}{t} - \frac{1}{\bar{t}}\right)^2 + \sum_{r=1}^{\infty} a^2_{rn-1} (t^{2rn-2} + \bar{t}^{2rn-2})\right.$$

$$+ \Sigma\, \Sigma\, a_{rn-1} a_{sn-1} (t^{rn+sn-2} + \bar{t}^{rn+sn-2})$$

$$\left. - 2 \sum_{m=1}^{\infty} \mathrm{K}_m (t^{nm} + \bar{t}^{nm})\right] + c. \tag{4.5}$$

Taking R, θ as the polar co-ordinates in the t-plane, we can write on the boundary of the unit circle $\mathrm{R} = 1$,

$$\psi = -\mathrm{U}\left[-\sin\theta + \sum_{r=1}^{\infty} a_{rn-1} \sin(rn-1)\theta\right]$$

$$- \tfrac{1}{4}\omega \left[\cos 2\theta + \sum_{r=1}^{\infty} a^2_{rn-1} \cos(2rn-2)\theta\right.$$

$$+ \Sigma\Sigma\, a_{rn-1}\, a_{sn-1} \cos(rn + sn - 2)\theta$$

$$\left. - 2 \sum_{m=1}^{\infty} \mathrm{K}_m \cos nm\theta\right] + c. \tag{4.6}$$

Therefore we take

$$\phi + i\psi = \mathrm{U}\left\{t - \sum_{r=1}^{\infty} a_{rn-1}t^{rn-1}\right\}$$

$$- \tfrac{1}{4}i\omega\left\{t^2 + \sum_{r=1}^{\infty} a^2{}_{rn-1}t^{2rn-2}\right.$$

$$\left. + \Sigma\Sigma\, a_{rn-1}a_{sn-1}t^{rn+sn-2} - 2\Sigma\, \mathrm{K}_m t^{nm}\right\}. \qquad (4.7)$$

Since

$$z^2 = \frac{1}{t^2} + \sum_{r=1}^{\infty} a^2{}_{rn-1}t^{2rn-2} + \sum_{r=0}^{\infty}\sum_{s=0}^{\infty} a_{rn-1}a_{sn-1}t^{rn+sn-2},$$

we can write

$$\phi + i\psi = \mathrm{U}\left\{-z + \left(t + \frac{1}{t}\right)\right\}$$

$$- \tfrac{1}{4}i\omega\left\{z^2 + t^2 - \frac{1}{t^2} - 2\sum_{m=1}^{\infty} \mathrm{K}_m t^{nm}\right\}. \qquad (4.8)$$

Therefore

$$\psi = -\mathrm{U}y + \mathrm{U}\left(\mathrm{R} - \frac{1}{\mathrm{R}}\right)\sin\theta$$

$$- \tfrac{1}{4}\omega\left\{x^2 - y^2 + \left(\mathrm{R}^2 - \frac{1}{\mathrm{R}^2}\right)\cos 2\theta\right.$$

$$\left. - 2\sum_{m=1}^{\infty} \mathrm{K}_m \mathrm{R}^{nm}\cos nm\theta\right\} \qquad (4.9)$$

Since on the boundary $\mathrm{R} = 1$ and

$$x^2 + y^2 = z\bar{z} = \Sigma\, a^2{}_{rn-1} + 2\sum_{m=1}^{\infty} \mathrm{K}_m \cos nm\theta,$$

the boundary condition is satisfied.

For the flow past the cylinder we get the stream function

$$\psi_1 = \mathrm{U}\left(\mathrm{R} - \frac{1}{\mathrm{R}}\right)\sin\theta - \tfrac{1}{4}\omega\left\{x^2 + y^2 + \left(\mathrm{R}^2 - \frac{1}{\mathrm{R}^2}\right)\cos 2\theta\right.$$

$$\left. - 2\sum_{m=1}^{\infty} \mathrm{K}_m \mathrm{R}^{nm}\cos nm\theta\right\}. \qquad (4.10)$$

5. *Liquid pressure on the cylinder.*—Let X, Y and M be the components along the axes and the moment about the origin of the pressure thrusts on

the cylinder. Then by an extension of Blasius' theorem for rotational flow, we have[4]

$$X - iY = \tfrac{1}{2} i\rho \int_c (u - iv)^2 \, dz \tag{5.1}$$

and

$$M = \text{real part of } -\tfrac{1}{2}\rho \int_c z\,(u - iv)^2 \, dz, \tag{5.2}$$

c being the boundary of the cylinder.

From (4.10) the stream function for the flow past the cylinder is the imaginary part of

$$U\left(t + \frac{1}{t}\right) - \tfrac{1}{4} i\omega \left\{x^2 + y^2 + t^2 - \frac{1}{t^2} - 2 \sum_{m=1}^{\infty} K_m t^{nm}\right\}.$$

The complex velocity at any point is therefore given by

$$u - iv = \tfrac{1}{2} i\omega \bar{z} - \left\{U\left(1 - \frac{1}{t^2}\right) - \tfrac{1}{2} i\omega \left(t + \frac{1}{t^3} - n \Sigma K_m m t^{nm-1}\right)\right\} \frac{dt}{dz}. \tag{5.3}$$

On the boundary

$$u - iv = \tfrac{1}{2} i\omega \sum_{0}^{\infty} a_{rn-1} t^{-rn+1} - \left\{U\left(1 - \frac{1}{t^2}\right) - \tfrac{1}{2} i\omega \left(t + \frac{1}{t^3} - n \sum_{1}^{\infty} K_m m t^{nm-1}\right)\right\} \frac{dt}{dz}. \tag{5.4}$$

If

$$G = \tfrac{1}{2} i\omega \sum_{0}^{\infty} a_{rn-1} t^{-rn+1}$$

$$H = U\left(1 - \frac{1}{t^2}\right) - \tfrac{1}{2} i\omega \left(t + \frac{1}{t^3} - n \Sigma K_m m t^{nm-1}\right),$$

$$X - iY = \tfrac{1}{2} i\rho \int_c \left(G^2 \frac{dz}{dt} + H^2 \frac{dt}{dz} - 2GH\right) dt \tag{5.5}$$

and

$$M = \text{real part of } -\tfrac{1}{2}\rho \int_c z \left(G^2 \frac{dz}{dt} + H^2 \frac{dt}{dz} - 2GH\right) dt. \tag{5.6}$$

Now

$$\int_c G^2 \frac{dz}{dt} \, dt = 0$$

and

$$\oint \mathrm{GH}\, dt = \pi\omega\,(\mathrm{U} + \tfrac{1}{8}\, i\omega) \qquad \text{when} \quad n = 3,$$
$$= \pi\omega\mathrm{U} \qquad \text{when} \quad n \geqslant 4.$$

We have

$$\frac{dz}{dt} = \frac{1}{t^2}\left\{-1 + \sum_{r=1}^{\infty} a_{rn-1}\,(rn-1)\,t^{rn}\right\}.$$

The series on the right is absolutely convergent for $|\,t\,| \leqslant 1$, and

$$\left|\sum_{1}^{\infty} a_{rn-1}\,(rn-1)\,t^{rn}\right| \;<\; \Sigma\;|\,a_{rn-1}\,(rn-1)\,|.$$
$$< 1.$$

Therefore

$$\frac{dt}{dz} = -\,t^2\Big[1 + \sum_{1}^{\infty} a_{rn-1}\,(rn-1)\,t^{rn}$$
$$+ \{\Sigma\, a_{rn-1}\,(rn-1)\,t^{rn}\}^2 + \ldots.\Big].$$

So we find

$$\int \mathrm{H}^2\,\frac{dt}{dz}\,dt = -\,2\pi\mathrm{U}\omega + \frac{\pi i}{3}\,\omega^2 \qquad \text{when} \quad n = 3,$$
$$= -\,2\pi\mathrm{U}\omega \qquad \text{when} \quad n \geqslant 4.$$

Therefore for all values of $n \geqslant 3$

$$\mathrm{X} - i\mathrm{Y} = -\,2\pi i\rho\mathrm{U}\omega$$

or

$$\mathrm{X} = 0, \quad \mathrm{Y} = 2\pi\rho\mathrm{U}\omega.$$

Thus we see that the force exerted is a lift force and is independent of the number of sides of the polygon.

The contribution to the real part from the first and third integrals in (5.6) is clearly zero. The contribution from the second integral is $2\pi\mathrm{U}\omega$ when $n = 3$ and it is zero when $n \geqslant 4$. Therefore the moment is $-\,\pi\rho\mathrm{U}\omega$ when $n = 3$, and it is zero when $n \geqslant 4$.

6. *Cylinder of hypotrochoidal cross-section.*—The transformation

$$z = \mu\left(\frac{1}{t} + mt^n\right), \quad \mu > 0, \quad 0 \leqslant m \leqslant \frac{1}{n}, \tag{6.1}$$

where n is a positive integer, transforms the outside of the hypotrochoid in the z-plane on to the interior of the unit circle in the t-plane. The

parametric representation of the curve in the z-plane corresponding to the circle $|t| = 1$ in the t-plane is given by

$$x = \mu(\cos\phi + m\cos n\phi)$$

$$y = \mu(-\sin\phi + m\sin n\phi). \tag{6.2}$$

If $m = 0$ the curve is a circle; if $n = 1$ the curve is an ellipse. When $n = 1/m = 2$ and $n = 1/m = 3$, the corresponding curves have three and four cusps respectively and they resemble in shape a triangle and a square respectively.

Proceeding in the same way as before, we get the stream function for the flow past the cylinder to be

$$\psi = \mu U\left(R - \frac{1}{R}\right)\sin\theta - \tfrac{1}{4}\omega\left[x^2 + y^2 + \mu^2\left\{\left(R^2 - \frac{1}{R^2}\right)\right.\right.$$

$$\left.\left.\times\cos 2\theta - 2mR^{n+1}\cos(n+1)\theta\right\}\right]. \tag{6.3}$$

The thrust on the cylinder for $n \geqslant 2$ and $mn = 1$ may be calculated as before. We find when $n = 2$,

$$X = -\tfrac{1}{2}\pi\rho\mu(U^2 + \tfrac{1}{2}\omega^2\mu^2),$$

$$Y = \tfrac{3}{4}\pi\rho\mu^2 U\omega;$$

when $n = 3$, $X = 0$,

$$Y = \tfrac{1}{3}\pi\rho\mu^2 U\omega;$$

when $n = 4$,

$$X = \tfrac{1}{8}\pi\rho\mu^3\omega^2, \qquad Y = \tfrac{7}{8}\pi\rho\mu^2 U\omega;$$

when $n \geqslant 5$,

$$X = 0,$$

$$Y = \left(1 - \frac{1}{2n}\right)\pi\rho\mu^2 U\omega.$$

The moment is found to be $-5/4\,\pi\rho\mu^3 U\omega$ when $n = 2$ and it is zero when $n \geqslant 3$.

Adjusting μ such that the arc length between two consecutive cusps of the hypotrochoid may correspond to the length of a side of the regular polygon, the results are tabulated below.

Cross-section	*Drag*	*Lift*	*Moment*
Equilateral triangle ..	0	$2\pi\rho U\omega$	$-\pi\rho U\omega$
Three-cusped hypotrochoid	$-(0\cdot445\pi\rho U^2 + 0\cdot176\pi\rho\omega^2)$	$0\cdot593\,\pi\rho U\omega$	$-0\cdot879\,\pi\rho U\omega$
Square	0	$2\pi\rho U\omega$	0
Four-cusped hypotrochoid	0	$0\cdot239\,\pi\rho U\omega$	0

In conclusion I wish to thank Prof. B. R. Seth for his kind guidance throughout the preparation of this paper.

2. Summary

The stream function for the rotational flow of liquid past a regular polygonal cylinder of n sides is obtained and the thrust on the cylinder due to liquid motion is calculated. It is found that the thrust is independent of the number of sides of the polygon when the length of a side is taken as $2d \sin(\pi/n)$, d being the radius of the circumscribed circle. Further, the corresponding problem for hypotrochoidal cylinders is also considered and the thrust is calculated in each case. The results for cross-sections of equilateral triangle and square are compared with those of hypotrochoids of three and four cusps respectively.

3. References

1. Mitchell, A. R. .. *Proc. Inter. Cong. Math.* (Amsterdam), 1954, **2**, 363.
2. Seth, B. R. .. *Jour. Lond. Math. Soc.*, 1939, **14**, 255.
3. De, K. .. *Bull. Cal. Math. Soc.*, 1954, **46**, 81.
4. ———— .. *Ibid.*, 1953, **45**, 121.

COMPLEX MAGNETIC PERMEABILITY TENSOR AND PARAMAGNETIC RESONANCE ABSORPTION IN $CuSO_4$ 5 H_2O

By (Miss) K. Sundaramma

(Department of Physics, Indian Institute of Science, Bangalore-3)

Received May 6, 1957

(Communicated by Prof. R. S. Krishnan, F.A.SC.)

1. Introduction

The present work is a continuation of the work reported by Sundaramma and Suryan (1957) on the values of absorption in $CuSO_4$ 5 H_2O. Copper sulphate has been investigated both for magnetic anisotropy (Krishnan and Mookerjee, 1936) and for paramagnetic resonance (Bagguley and Griffiths, 1950), (Arnold and Kip, 1949). The present work is concerned with the determination of the absolute values of paramagnetic resonance absorption in single crystals of copper sulphate in various directions. The permeability tensor can be represented by $\chi = \chi' + i\chi''$ and χ'' is measured by resonance methods.

2. Magnetic Properties of Copper Sulphate

(*a*) *The magnetic axes and the choice of crystal orientations for the study of* χ''.—As already mentioned there has been considerable data on copper sulphate. All the available data go to prove that each of the two inequivalent copper ions has a tetragonal field around it and the angle between the tetragonal axes being about 100°. There is some diversity of notation employed for denoting the various magnetic axes of the crystal among various workers. Table I summarises the notation.

The co-ordinates of the above directions with respect to the crystallographic axes are as follows:—

L_1 (154°, 64°, 51°); L_3 (66°, 86°, 42°);
L_2 (78°, 130°, 52°); L_3' (85°, 22°, 100°);
L_4 (70°, 41°, 69°).

The notations used in giving the co-ordinates are as used in the present investigation.

Figure 1 gives a stereographic projection of the crystal about the '*C*' axis, which is invaluable for choosing and visualizing the crystal orientation and

TABLE I

Table of Notation

Name	Tetragonal axis 1	Tetragonal axis 2	Normal to the plane containing tetragonal axes	Internal bisector of tetragonal axes	External bisector of tetragonal axes
Bagguley and Griffiths (1950)	L_2	L_4	L_1	..	L_3
Krishnan and Mookerjee (1936)	Z_1	Z_2	α	β	γ
Arnold and Kip (1949)	..	..	γ	β	α
Present Paper	L_2	L_4	L_1	L_3'	L_3

the direction of the magnetic axes. It is seen from previous data that there is practically no variation of *g*-value in the plane containing the two tetragonal axes and the *g*-value is maximum in that plane. In a direction normal to the plane the *g*-value is minimum and the paramagnetic resonance line is

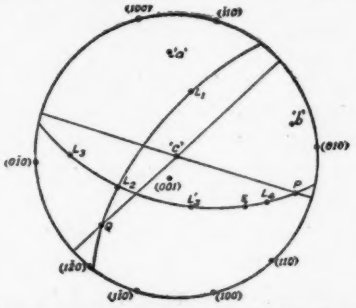


FIG. 1. Stereographic projection of $CuSO_4\ 5\,H_2O$ about the '*C*' axis.

sharp. The susceptibility also behaves similarly and the crystal of copper sulphate though triclinic crystallographically behaves like a uniaxial crystal so far as magnetic susceptibility is concerned and the unique axis being the L_1 direction.* The L_1 direction is approximately in the OCP_1 zone of the crystal and is about 9° away from the '0' direction and towards the $(1\bar{1}0)$ direction. The plane L_1L_2 contains one of the tetragonal axes and the normal to the plane of the tetragonal axes. Its zone axis is denoted by

* The L_1, L_2, L_3' and L_4 are the various magnetically important axes.

'ξ' in Fig. 1. In the listing of the co-ordinates by Bagguley and Griffiths the co-ordinates of L_4 are erroneously given for L_3 and their definition of internal bisector does not agree with that ordinarily understood. Thus the L_3 defined by them is the line bisecting the 80° angle between the two tetragonal axes rather than the supplement 100° angle one measures when going from the positive direction of L_2 to positive direction of L_4. The $L_1 L_2$ and the $L_2 L_4$ planes are the ones investigated for the absolute values paramagnetic resonance absorption besides a few other arbitrary planes for check.

(*b*) *The methods of measuring the values of* χ''.—As already pointed out the existing data on paramagnetic substances are mostly in arbitrary units and they do not permit comparison among one another or even among the different directions of the same crystal. The absolute values of paramagnetic resonance absorption are available only for a few crystalline powders in the original work of Cummerow and Halliday (1947). Subsequently, the Japanese workers (Kumagai and others, 1954) have tried to find validity of Kramers-Kronig relation by making measurements of $MnSO_4.H_2O$ and the L_1 direction of $CuSO_4\,5\,H_2O$. The earlier methods involve the measurement of the Q of the cavity resonator and the results depend upon the form factor which is not easily evaluated. The use of the cavity Q method for the innumerable directions of single crystals would be tedious and a simple and relatively less means of finding the absorption would be of advantage. Such a method has been tried successfully for several powders and the results have been given in a previous paper (Sundaramma, 1956). The method in brief consists in comparing the value of absorption of a suitably chosen standard substance (whose absorption can be determined accurately by other methods once and for all). The method requires accurate absorption curves if serious errors are to be avoided. As has been pointed out in that paper in the section on experimental details, a number of precautions have to be taken to ensure satisfactory results.

3. CRYSTAL SPECIMENS

The specimens for investigation were cut and ground from good single crystals of copper sulphate. In the $L_2 L_4$ plane the direction represented by R in Fig. 1 (*i.e.*, the intersection of the trace of the 100 plane with the trace of $L_2 L_4$ plane) was used as a reference direction. The angular distance between R and L_2 is about 30°. The $L_1 L_2$ plane cuts (110) plane at Q in Fig. 1 and this direction was used for reference in the $L_1 L_2$ plane. L_2 and Q are 25° from each other.

4. Results

Complete mesurements of paramagnetic resonance peak value, the absorption curve and the absorption curve with manganous sulphate as standard substance have been taken in both the planes at close enough intervals varying from 5° to 15°. From these the *g*-values, line width, peak absorption integrated absorption and the integral occurring in the Kramers-Kronig relation have all been calculated.

The results have been presented in Figs. 2 and 3. Of these the *g*-values agree well with those of the previous workers. The half-widths found in this investigation are generally somewhat smaller than those reported by Bagguley and Griffiths presumably because of the difference in the frequencies of observation (the wave-length being 3·04 cm. by Bagguley and Griffiths and 3·4 cm. in the present case). The results on the absolute values of absorption and its variation with direction are entirely new and hence cannot be compared and are presented here for the first time.

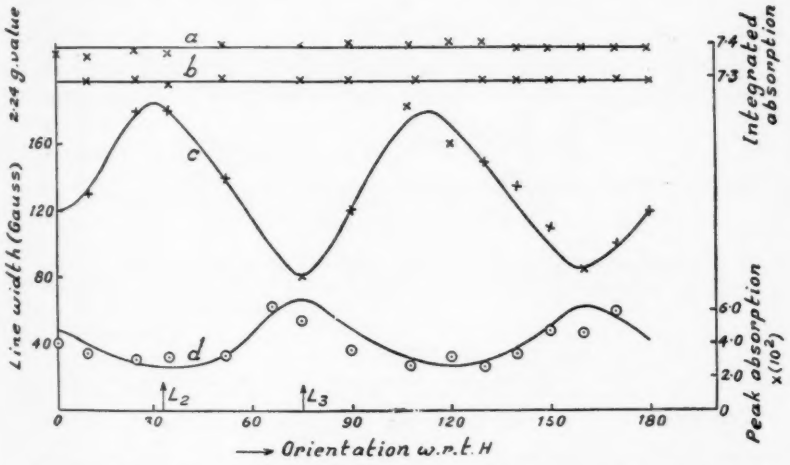


Fig. 2. Experimental curves for the peak absorption and integrated absorption in the L_2L_3 plane. (*a*) Integrated absorption, (*b*) *g*-value, (*c*) line width, (*d*) peak absorption.

It is found that the values (peak values) range from about 2×10^{-2} cm.^{3} per mole, the peak absorption in the L_2 direction to 8×10^{-2} cm.^{3}, the greatest in the L_1 direction (the line being extremely narrow 50 oersteds full width at half power owing to exchange interaction). The total, *i.e.*, the integrated absorption is practically constant in the L_2 L_4 plane and that in the L_1 L_2 plane shows a slight minimum in the L_1 direction. Thus the shape of the

absorption ellipsoid is that of slightly elongated sphere. Within the limits of the experimental error (estimated to be a few per cent. overall) the direction of the unique axis for χ'' is the same as that for χ'. It is found that the Kramers-Kronig relation between zero field susceptibility and the absorption curve is satisfied in all cases within the limits of experimental error. Table II summarises the values of absorption per mole (peak and integrated) for the directions L_1, L_2, L_3 and L_4 in the crystal.

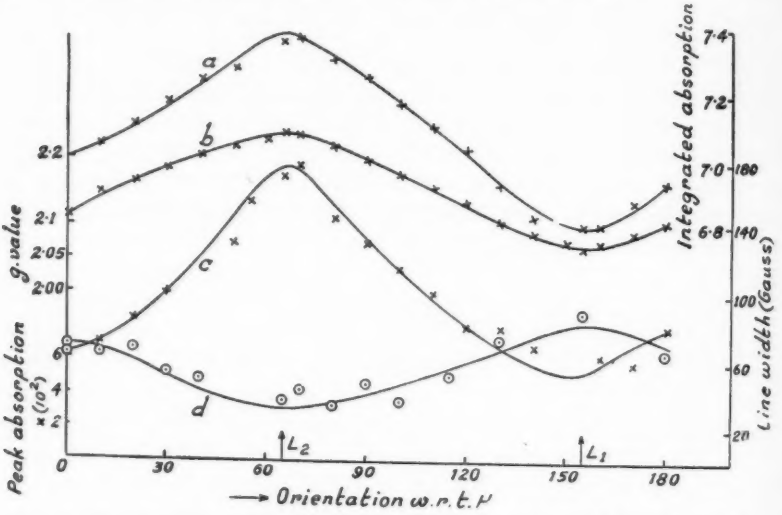


FIG. 3. Experimental curves for the peak absorption and integrated absorption in the L_1L_2 plane. (*a*) Integrated absorption, (*b*) *g*-value, (*c*) line width, (*d*) peak absorption.

TABLE II

Direction	L_1	L_2	L_3	L_4	Powder
Absorption peak value $\times 10^2$	7·9	3·24	5·9	2·98	2·40
Integrated Absorption	6·81	7·37	7·39	7·38	7·40

The values in the directions L_1 and L_2 may be taken as the principal values of the integrated absorption ellipsoid. Before concluding it should be emphasised that the absorption here measured is the resonant part alone and does not include non-resonant absorption at low fields that due to other

causes. The peak absorption values are in units of $10^{-2} \times$ cm.^{3} The total absorption values are in cm.^{3} gauss.

Summary

The paper presents the result of work done in order to investigate the intensity and comparison of intensities in paramagnetic resonance absorption in several directions of a single crystal of copper sulphate. It was the object of this investigation to see if the absorption tensor was also represented by an ellipsoid of revolution and if so to find the principal values of the tensor. It is found that the peak absorption is not represented by an ellipsoid of revolution. The total or integrated absorption is uniaxial and almost spherical.

Acknowledgement

The author is thankful to Professor R. S. Krishnan for his keen interest in the progress of the work and Dr. G. Suryan for valuable suggestions.

References

1. Arnold, R. and Kip, A. .. *Phys. Rev.*, 1949, **75**, 1199.
2. Bagguley, D. M. S. and Griffiths, J. H. E. *Proc. Roy. Soc.* (*London*), 1950 *a*, **201**, 366.
3. Cummerow, R. L., Halliday, D. and Moore, G. E. *Phys. Rev.*, 1947, **72**, 173.
4. Krishnan, K. S. and Mookerjee, A. *Ibid.*, 1936, **50**, 860.
5. ———— .. *Ibid.*, 1938, **54**, 533.
6. Kumagai, H., Hayashi, I., Ono, K., Abe, H., Shimada, J. and Shono, H. *J. Phys. Soc., Japan*, 1954, **9**, 376.
7. Sundaramma, K. .. *Proc. Ind. Acad. Sci.*, 1956, **44 A**, 345.
8. ——— and Suryan, G. .. *Curr. Sci.*, March 1957.

SELECTIVE DEMETHYLATION OF THE 5-METHOXYL GROUP IN FLAVANONES AND SYNTHESIS OF DIHYDROWOGONIN

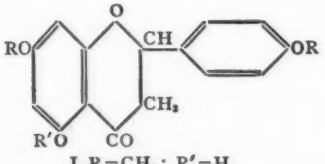
By S. N. Aiyar, Ishwar Dass and T. R. Seshadri, F.A.Sc.

(Department of Chemistry, University of Delhi, Delhi)

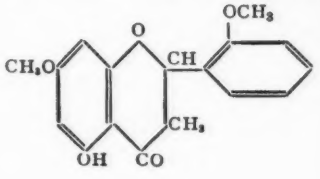
Received June 8, 1957

A convenient method was needed for the exclusive demethylation of the 5-methoxyl group in flavanones. Aluminium chloride in nitrobenzene and hydrobromic acid which are satisfactory in simpler cases are not suitable for more complex flavanones because they can demethylate other positions also; further, hydrobromic acid can bring about ring isomeric change. Aqueous hydrochloric acid, which has been used in the case of furanochromones[1] and isoflavones,[2] has not been successful in the partial demethylation of flavanones. On the other hand, aluminium chloride in dry ethereal solution serves the purpose very well and gives good yields. By means of this reagent a number of representative methoxy flavanones have now been converted into the corresponding 5-hydroxy compounds. This reagent was earlier used by Baker and Simmonds[3] for the preparation of 5-hydroxy-8:4′-dimethoxy flavone, and has not so far been employed in the flavanone series.

The reagent was first tested in simple cases for the preparation of known compounds. 5-Hydroxy flavanone[4] is smoothly prepared by the demethylation of 5-methoxy flavanone. The product is found to be identical with the sample obtained by the action of hydrobromic acid on 2-hydroxy-6-methoxy chalkone whereby demethylation and ring closure are known to take place.[5] 5-Hydroxy-7-methoxy flavanone was prepared earlier from 5:7-dimethoxy-flavanone by demethylation with aluminium chloride and nitrobenzene[6]; aluminium chloride in ether is much better. Naringenin dimethyl ether[7] (I) originally obtained by the partial methylation of naringenin (II) with diazomethane is also formed easily from the trimethyl ether (III) by the partial demethylation. Under this category comes citronetin methyl ether also[8] (IV).

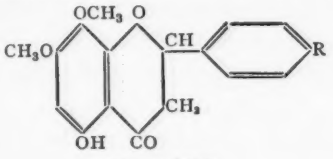


I R=CH_3; R′=H
II R=R′=H
III R=R′=CH_3

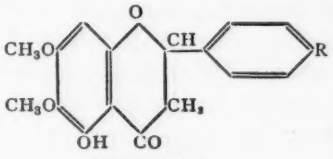


IV

For the study of carthamidin (5:7:8:4′-tetrahydroxy flavanone) and isocarthamidin (5:6:7:4′-tetrahydroxy flavanone) and the recently discovered dihydrowogonin[9] (5 : 7-dihydroxy-8-methoxy flavanone), convenient derivatives, which can be used for comparison, are the partial methyl ethers with only the 5-hydroxyl group left free. They are usually made by carrying out the partial methylation of the natural hydroxy flavanones with diazomethane or with restricted quantities of dimethyl sulphate. Authentic samples of synthetic compounds can now be easily obtained for comparison by the partial demethylation of synthetic methyl ethers using aluminium chloride in ether solution. As typical examples, carthamidin trimethyl ether (5-hydroxy-7:8:4′-trimethoxy flavanone, V), isocarthamidin trimethyl ether (5-hydroxy-6:7:4′-trimethoxy flavanone, VI), dihydrowogonin monomethyl ether (5-hydroxy-7:8-dimethoxy flavanone, VII) and also 5-hydroxy-6:7-dimethoxy flavanone (VIII) have been prepared by partial demethylation.

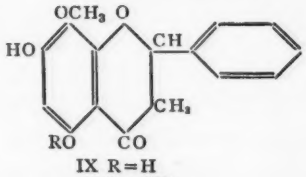


V R=OCH_3
VII R=H



VI R=OCH_3
VIII R=H

The method can be conveniently used also for the preparation of certain naturally occurring flavanones. As an example, the synthesis of dihydrowogonin[9] (IX) has now been carried out. For this purpose 7-hydroxy-5:8-dimethoxy flavanone (X) has been prepared by the condensation of 2:4-dihydroxy-3 : 6-dimethoxy acetophenone[10] and benzaldehyde and subsequent ring closure. This undergoes smooth demethylation with aluminium chloride in ether and the product is found to be identical with dihydrowogonin (IX), isolated from *Prunus avium* by Mentzer *et al.*,[9] in all its properties and reactions except optical activity. The partial methyl ether (7-methyl ether) of the synthetic compound has been made by means of diazomethane and is found to be identical with a similar sample prepared from natural dihydro-



IX R=H
X R=CH_3

wogonin[11] and also with the synthetic 5-hydroxy-7 : 8-dimethoxy flavanone (VII) mentioned earlier. These observations confirm that there has been no isomeric change during the demethylation in ether solution.

Recently Chopin *et al.*[12] condensed iretol with cinnamoyl chloride in the presence of aluminium chloride and could isolate the isomeric dihydro-oroxylin from the product. They proved the presence of dihydrowogonin in the more soluble fractions by chromatography. Our method is quite convenient for the synthesis of dihydrowogonin.

EXPERIMENTAL

General method of selective demethylation of the 5-methoxyl group

The 5-methoxy flavanone is dissolved or suspended as very fine powder in anhydrous ether, powdered anhydrous aluminium chloride added in excess and the mixture stirred for ten minutes and kept at room temperature for about twenty-four hours. Ether is then distilled off and the aluminium chloride complex decomposed with ice-cold hydrochloric acid which is subsequently warmed if necessary for half an hour to complete the decomposition. The solid that separates is filtered and washed with water and crystallised from a suitable solvent.

5-*Hydroxy flavanone.*—(*a*) Demethylation of 5-methoxy flavanone as given above yielded a product which crystallised from alcohol yielding colourless broad rectangular plates, m.p. 63–64° (Found: C, 74·6; H, 5·0; $C_{15}H_{12}O_3$ requires C, 75·0; H, 5·0%). It gives a deep reddish violet colour with ferric chloride in alcoholic solution and with concentrated nitric acid a permanent green solution. Though the properties and analysis agree with the previous description of 5-hydroxy flavanone,[4] the melting point observed now is considerably lower. The earlier sample was not available, and the earlier method does not give consistent results. However, demethylation of 2-hydroxy-6-methoxy chalkone as given below yielded the same product, m.p. 63-64°, and hence there was no doubt about the correctness of the present sample.

(*b*) *Demethylation of 2-hydroxy-6-methoxy chalkone with hydrobromic acid.*—The chalkone (0·5 g.) was treated with a saturated solution of hydrobromic acid in acetic acid (10 c.c.) and the red solution heated on a boiling water-bath for two hours. It was then diluted with water (50 c.c.) when a dark brown semi-solid separated. This was ether extracted, the extract washed with cold aqueous sodium carbonate (2%) and dried over anhydrous sodium sulphate. The solvent was distilled off and the residue crystallised from ethyl acetate-petroleum ether mixture and then from methanol. It

separated as colourless broad rectangular plates, m.p. 63–64°, undepressed by admixture with the sample from (*a*).

5-Hydroxy-7-methoxy flavanone

The product obtained by the demethylation of 5 : 7-dimethoxy flavanone with aluminium chloride crystallised from alcohol as colourless prisms, m.p. 100–01°, undepressed by an authentic sample of 5-hydroxy-7-methoxy flavanone.[6] It gave a red colour with ferric chloride in alcoholic solution and a green colour with concentrated nitric acid which rapidly changed to blue.

5-Hydroxy-7 : 4′-dimethoxy flavanone (*Naringenin dimethyl ether*)

This was prepared in a similar way from 5 : 7 : 4′-trimethoxy flavanone. It crystallised from ethyl acetate as colourless long rectangular prisms, m.p. 120–22°, either alone or with naringenin 7 : 4′ dimethyl ether.[7] It gave a red colour with ferric chloride in alcoholic solution and a blue colour with concentrated nitric acid. It developed a brilliant purple colour with magnesium and hydrochloric acid.

5-Hydroxy-7 : 2′-dimethoxy flavanone (*Citronetin monomethyl ether*)

5 : 7 : 2′-Trimethoxy flavanone underwent smooth demethylation and the product crystallised from ethyl acetate-petroleum ether mixture and then from absolute alcohol as colourless rectangular tablets, m.p. 91–92° either alone or with an authentic sample of citronetin monomethyl ether.[8] It gave a wine red colour with ferric chloride and a deep blue colour with concentrated nitric acid. It developed a pink colour with magnesium and hydrochloric acid.

5-Hydroxy-7 : 8-dimethoxy flavanone

5 : 7 : 8-Trimethoxy flavanone was subjected to selective demethylation and in this case the product was extracted with benzene and the benzene layer washed with hydrochloric acid and then with water. It was dried over anhydrous sodium sulphate, the solvent distilled off and the residue crystallised from methanol yielding colourless rectangular prisms melting at 98–99°. The substance gave a green colouration with ferric chloride in alcoholic solution. With concentrated nitric acid it developed an orange red colour (Found: C, 68·6; H, 5·0; $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·3%).

5-Hydroxy-7 : 8 : 4′-trimethoxy flavanone (*Carthamidin trimethyl ether*)

This was obtained by the general method from 5 : 7 : 8 : 4′-tetramethoxy flavanone. It crystallised from methanol as pale yellow broad and thin

plates melting at 137–38°. Its alcoholic solution gave a greenish brown colour with ferric chloride and a magenta colour with magnesium and hydrochloric acid. With concentrated nitric acid it developed an orange colour (Found: C, 64·4; H, 5·7; $C_{18}H_{18}O_6$ requires C, 65·4; H, 5·4%).

5-Hydroxy-6 : 7-dimethoxy flavanone

This resulted from the demethylation of 5 : 6 : 7-trimethoxy flavanone and crystallised from alcohol as colourless rectangular plates, m.p. 148–50°. It gave a red colour with ferric chloride in alcoholic solution changing with excess to greenish brown. With concentrated nitric acid, it developed a wine red colouration (Found: C, 67·7; H, 5·4; $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·3%).

5-Hydroxy-6 : 7 : 4′-trimethoxy flavanone (*Isocarthamidin trimethyl ether*)

This was obtained in good yield from 5 : 6 : 7 : 4′-tetramethoxy flavanone and it crystallised from alcohol as pale yellow rectangular prisms, m.p. 132–33°. It gave a reddish violet colour with alcoholic ferric chloride changing gradually to green. With concentrated nitric acid it developed an orange red colour, and with magnesium and hydrochloric acid a purple colour (Found: C, 64·8; H, 5·5; $C_{18}H_{18}O_6$ requires C, 65·4; H, 5·4%).

7-Hydroxy-5 : 8-dimethoxy flavanone

To a solution of 2 : 4-dihydroxy-3 : 6-dimethoxy acetophenone[10] (0·5 g.) in alcohol (5 c.c.), benzaldehyde (redistilled; 0·3 g.) in alcohol (2 c.c.) and saturated alcoholic potash (5 c.c.) were added and the mixture kept at room temperature (25° C.) for 48 hours. It was then diluted with 30 c.c. of water and ether extracted to remove unchanged aldehyde. The aqueous solution on acidification deposited a brown oil which soon solidified on stirring to an yellow-brown solid. It was macerated with sodium bicarbonate solution, filtered and the residue crystallised from ethyl acetate yielding very pale yellow large rectangular prisms, m.p. 185–86°. Yield 0·3 g. (Found: C, 67·9; H, 5·9; $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·3%). There was no change when it was heated with alcoholic sulphuric acid and it should therefore be the flavanone.

5 : 7-Dihydroxy-8-methoxy flavanone (*Dihydrowogonin*)

7-Hydroxy-5 : 8-dimethoxy flavanone (0·15 g.), ether (5 c.c.) and anhydrous aluminium chloride (0·5 g.) were stirred for 12 hours using magnetic stirrer and the mixture allowed to stand at room temperature (25° C.) for 36 hours. Ether was distilled off and the brownish aluminium chloride complex decomposed with ice-cold hydrochloric acid (1 : 1) and the decom-

position completed by warming on a water-bath to 45° C. The pale yellow product was extracted with benzene, and the benzene layer washed with dilute hydrochloric acid and then with water, dried and concentrated when the flavanone crystallised out. Recrystallisation from benzene yielded rectangular tablets, m.p. 147–48°, undepressed by admixture with the natural sample of dihydrowogonin (m.p. 148°) (yield 0·1 g.) (Found: C, 66·9; H, 5·4; OCH_3, 10·8. $C_{16}H_{14}O_5$ requires C, 67·1; H, 4·9; 1 OCH_3, 10·8%).

It gave a pinkish brown colour with ferric chloride, a red colour with concentrated nitric acid and an yellow-orange colour with magnesium and hydrochloric acid agreeing with the behaviour of natural dihydrowogonin.

Dihydrowogonin monomethyl ether

Synthetic dihydrowogonin (0·05 g.) was dissolved in ether (10 c.c.) and a solution of diazomethane in ether (1·5 moles) was added. This mixture was left in the refrigerator overnight, ether distilled off and the yellow residue crystallised from methyl alcohol yielding long rectangular prisms, m.p. 98°, undepressed by admixture with the same methyl ether similarly prepared from natural dihydrowogonin[11] and also with 5-hydroxy-7: 8-dimethoxy flavanone already described.

We convey our thanks to Prof. C. Mentzer and Dr. J. Chopin for the gift of natural dihydrowogonin and its 7-methyl ether.

Summary

Anhydrous aluminium chloride in ether solution is found to be a convenient reagent for the selective demethylation of the 5-position of methoxy flavanones and these 5-hydroxy compounds can serve as standard derivatives for comparison. A number of typical compounds are reported, the most important being naringenin dimethyl ether, citronetin monomethyl ether and carthamidin and isocarthamidin trimethyl ethers. The method has been employed for the synthesis of dihydrowogonin which has been recently isolated. This involves the preparation and partial demethylation of 7-hydroxy-5: 8-dimethoxy flavanone.

References

1. Schönberg and Badran .. *J.A.C.S.*, 1951, **73**, 2960;
   Mukerjee and Seshadri .. *Proc. Ind. Acad. Sci.*, 1952, **35 A**, 326.
2. Dhar *et al.* .. *Journ. Sci. Ind. Res.*, 1955, **14 B**, 73;
   Mahesh *et al.* .. *Proc. Ind. Acad. Sci.*, 1954, **39 A**, 166.
3. Baker and Simmonds .. *J.C.S.*, 1940, 1373.

4. Narasimhachari and Seshadri .. *Proc. Ind. Acad. Sci.*, 1948, **27 A**, 236.
5. ——— .. *Ibid.*, 1949, **29 A**, 265;
   ——— .. *Ibid.*, 1950, **32 A**, 21.
6. Rao and Seshadri .. *Ibid.*, 1946, **23 A**, 213.
7. Shinoda and Sato .. *J. Pharm. Soc., Japan*, 1928, **48**, 933;
   Narasimhachari and Seshadri .. *Proc. Ind. Acad. Sci.*, 1948, **27 A**, 234.
8. Shinoda and Sato .. *Chem. Abs.*, 1932, **26**, 1916;
   Narasimhachari *et al.* .. *Proc. Ind. Acad. Sci.*, 1953, **37 A**, 626.
9. Mentzer *et al.* .. *Bull. Soc. Chim. Biol.*, 1954, **36**, 1137;
   Chopin *et al.* .. *Compt. Rend.*, 1956, **243**, 712.
10. Wesseley and Moser .. *Monatsh.*, 1930, **56**, 97.
11. Chopin and Delepine .. *Compt. Rend.*, 1956, **243**, 745.
12. Molho *et al.* .. *Ibid.*, 1957, **244**, 470.

CRYSTALLINE CHEMICAL COMPONENTS OF THE LEAVES OF *RHODODENDRON FALCONERI* HOOK.

By S. Rangaswami, F.A.Sc. and K. Sambamurthy
(*Department of Pharmacy, Andhra University, Waltair*)

Received June 24, 1957

Rhododendron leaves are generally considered to be poisonous to cattle and sheep. *Rhododendron falconeri* is reported by Plugge[1] to contain the toxic substance andromedotoxin. Chopra[2] mentions the plant as a fish poison. The plant grows in the Himalayas from Nepal to Bhutan at altitudes from 9,000 to 13,000 ft. and has been described in the monograph *Poisonous Plants of India* by Chopra, Badhwar and Ghosh.[3] There is no record of chemical work on this species other than what has been mentioned above. We have therefore examined the leaves with a view to isolate the crystalline components thereof.

The powdered leaves were extracted with petroleum ether, ether and alcohol in succession. The petroleum-ether extract yielded, besides a large amount of wax, three crystalline substances, A, B and C, all of them in very poor yield. The ether extract yielded ursolic acid as the crystalline component in fairly good yield. From the alcoholic extract quercetin was obtained both before and after hydrolysis with mineral acid indicating that the pigment may be present in the plant material both in the free form and as glycoside.

The three crystalline substances obtained from the petroleum-ether extract appear to be triterpenoid in nature. Substance A which seems to be isomeric with α- and β-amyrins gave neither an acetate nor a 2: 4-dinitrophenylhydrazone. But it underwent isomerization on treatment with mineral acids. Substance B, whose analysis corresponds to that of a hydrocarbon, seems to be a new entity, while Substance C agrees with skimmiol (isolated from *Skimmia japonica*[4]) in its melting point and analysis. Dearth of material prevented any work on these three substances.

The identity of ursolic acid was established by its conversion into the acetate, the methyl ester, the acetate of the methyl ester, the benzoate of the methyl ester and methyl ursonate. Their physical constants agreed with values described in the literature[5–7] except in the case of the methyl ester where our preparation has a lower melting point than described in the literature[8]; the optical rotation however agrees with the literature value.[9]

Quercetin was characterized as its penta-acetate and pentamethyl ether. The combustion values for the pigment obtained from the extract were not entirely satisfactory, but the preparation obtained by hydrolysing the purified acetate was quite satisfactory in every respect. The details are given in the experimental portion.

EXPERIMENTAL

The coarsely powdered leaves (650 g.) were extracted under reflux with petroleum ether (4×2 litres). The petroleum ether-free powder was next extracted with ether (5×2 litres) and then with alcohol (3×2 litres) under reflux.

Petroleum-ether extract.—The combined extract, on concentration and keeping in the ice-chest, deposited a large amount of wax. This was filtered and the filtrate evaporated to a thick consistency. When the residue was set aside for about two months, it deposited a small amount of crystalline solid. On treatment with warm acetone the crystals remained insoluble, but the amorphous portion went into solution (Solution X, see later). The crystalline portion was separated by fractional crystallization from benzene-acetone into two fractions, one melting at about 198° and the other at about 232°. The former fraction, on recrystallization from benzene, separated as long needles (Substance A: 300 mg.) melting at 198°; $[\alpha]_D^{29} = +71{\cdot}9° \pm 3°$ (c = 0·873 in chloroform) (Found on sample dried *in vacuo* for 2 hrs. at 105°: C, 84·7; H, 12·0. $C_{30}H_{48}O$ requires: C, 84·8; H, 11·4%). With conc. sulphuric acid the substance gave a deep yellow colour changing to light orange and then to light pink; in the Liebermann-Burchard test it showed a pink colour.

Isomerization.—To a solution of the substance (25 mg.) in absolute alcohol (5 c.c.), conc. hydrochloric acid (4 drops) was added. After refluxing for ½ hr. the solution was diluted with water (5 c.c.) when a precipitate separated. This was filtered, washed free from acid and dried in the desiccator. On crystallization from benzene-acetone it separated as thin lustrous plates (20 mg.), m.p. 248–50°; $[\alpha]_D^{30} = -30{\cdot}5° \pm 2°$ (c = 0·452 in chloroform) (Found on sample dried *in vacuo* for 2 hrs. at 105°: C, 84·3; H, 11·8. $C_{30}H_{48}O$ requires: C, 84·8; H, 11·4%). The colour reactions were identical with those of the parent substance. The same product was obtained when in the above experiment conc. hydrochloric acid was substituted by 60% sulphuric acid.

The fraction melting at about 232° on recrystallization from benzene-petroleum ether separated as fine needles (Substance B: 100 mg.) melting at

232–34° (Found: C, 87·7; H, 12·2. $C_{30}H_{48}$ requires: C, 88·2; H, 11·8%). It gave a yellow colour with conc. sulphuric acid and a pink colour in the Liebermann-Burchard test.

The wax that separated from the petroleum-ether concentrate was warmed with excess of petroleum ether when most of it went into solution (Solution Y) leaving behind a small quantity of granular powder. This on filtering and crystallizing from benzene-methanol and benzene melted at 279–80° (Substance C: 75 mg.) (Found: C, 85·3; H, 12·3. $C_{30}H_{50}O$ requires: C, 84·5; H, 11·8%). It gave the usual triterpenoid colour reactions.

Solutions X and Y were mixed and evaporated to a syrupy residue which was saponified with N alcoholic potash and the unsaponifiable matter was extracted in the usual way. This on crystallization from absolute alcohol yielded some more quantity (120 mg.) of Substance A.

Ether extract: ursolic acid.—The combined extract on concentration to 200 c.c. deposited a pale greenish solid. This was filtered and repeatedly crystallized from benzene-methanol and absolute alcohol, when it separated as colourless needles, m.p. 266–68° (2·6 g.). The ethereal filtrate was poured into excess of petroleum ether when a greenish solid separated. This on crystallization from benzene-methanol gave colourless plates (3·6 g.), m.p. 261–65°. A further quantity (0·2 g.) of the same substance was obtained on evaporating the petroleum-ether filtrate to a syrupy residue, extracting with hot methanol, treating the mixed methanolic extract with charcoal, filtering and concentrating the filtrate. All the above three fractions were identical (mixed melting point and colour reactions) and were therefore mixed and recrystallized from benzene-methanol, when colourless plates, m.p. 266–68°, were obtained; $[\alpha]_D^{29} = +64·6° \pm 3°$ ($c = 0·692$ in absolute alcohol) [Found: C, 79·1; H, 11·0. $C_{30}H_{48}O_3$ (ursolic acid) requires: C, 78·9; H, 10·6%]. With conc. sulphuric acid it gave a yellow colour slowly changing to violet and in the Liebermann-Burchard test it gave a red colour changing to violet, then blue and finally green.

Derivatives of ursolic acid.—The acetate, prepared by heating the substance with acetic anhydride and fused sodium acetate, crystallized from alcohol as colourless needles, m.p. 281–83°; $[\alpha]_D^{28} = +64·3° \pm 3°$ ($c = 1·048$ in chloroform) [Found: C, 77·5; H, 10·4. $C_{32}H_{50}O_4$ (ursolic acid acetate) requires: C, 77·1; H, 10·1%].

The methyl ester (diazomethane method) crystallized from petroleum ether as clusters of feathery needles, m.p. 110–12°; $[\alpha]_D^{28} = +60·8° \pm 2°$

(c = 0·670 in pyridine) [Found on sample dried at 90° for 3 hrs. under vacuum: C, 79·6; H, 10·1; $-OCH_3$, 7·3. $C_{31}H_{50}O_3$ requires: C, 79·1; H, 10·7; $-OCH_3$ (1), 6·6%].

The acetate of the methyl ester, prepared from the methyl ester with acetic anhydride and sodium acetate, crystallized from alcohol as rectangular rods, m.p. 243–45°; $[\alpha]_D^{28} = +63·7° \pm 3°$ (c = 0·662 in chloroform) [Found: C, 76·6; H, 10·2; $-OCH_3$, 6·0. $C_{33}H_{52}O_4$ requires: C, 77·3; H, 10·2; $-OCH_3$ (1), 6·1%].

The benzoate of the methyl ester prepared from the methyl ester with pyridine and benzoyl chloride crystallized from chloroform-methanol as colourless plates, m.p. 213°; $[\alpha]_D^{28} = +72·8° \pm 2°$ (c = 0·893 in pyridine) (Found: C, 80·3; H, 9·8. $C_{38}H_{54}O_4$ requires: C, 79·4; H, 9·5%).

Methyl ursonate prepared by treating a glacial acetic acid solution of methyl ursolate with chromic acid and purified by chromatography over alumina crystallized from chloroform-acetone as prisms, m.p. 192°; $[\alpha]_D^{30} = +83·3° \pm 1°$ (c = 2·262 in pyridine) (Found: C, 80·0; H, 10·8. $C_{31}H_{48}O_3$ requires: C, 79·4; H, 10·3%).

Alcoholic extract.—The combined extract was concentrated to 200 c.c. and the concentrate poured into excess of ether (500 c.c.) whereby two immiscible layers were obtained.

The lower layer was diluted with water and hydrolysed by boiling with sulphuric acid (effective concentration 7%) for 2 hrs. The dark brown precipitate that separated on cooling (13 g.) could not be crystallized. The aqueous filtrate was extracted with ether, the extract washed neutral, dried and evaporated. On crystallizing the residue from alcohol yellow needles (1 g.), m.p. 296–98°, were obtained.

The ether layer was shaken with 5% potassium hydroxide solution and the separated alkaline solution neutralized with acid. On allowing to stand, the solution first deposited some sticky impurities and then a pale yellow substance which was identical with the substance obtained by the hydrolysis described above.

Penta-acetyl-quercetin prepared from the above crystallized from alcohol as woolly needles, m.p. 194° [Found: C, 58·7; H, 4·0; $-COCH_3$, 45·0. $C_{25}H_{20}O_{12}$ requires: C, 58·6; H, 3·9; $-COCH_3$ (5), 42·0%].

The acetate was deacetylated by dissolving the substance (60 mg.) in alcohol (5 c.c.), adding 20 c.c. of N sulphuric acid and refluxing for 18 hrs. The solution was cooled when the pigment precipitated out. It was filtered, washed and crystallized from aqueous methanol and aqueous acetone, when

it separated as fine needles, m.p. 318–22° (Found on sample dried *in vacuo* for 4 hrs. at 105°: C, 59·4; H, 3·8. $C_{15}H_{10}O_7$ requires: C, 59·6; H, 3·3%).

The pentamethyl ether of quercetin, prepared by the action of dimethyl sulphate and anhydrous potassium carbonate in acetone solution, crystallized from dilute alcohol as needles, m.p. 150–51° [Found: C, 64·7; H, 5·7; $-OCH_3$, 40·3. $C_{20}H_{20}O_7$ requires: C, 64·5; H, 5·4; $-OCH_3$ (5), 41·7%].

Summary

The leaves of *Rhododendron falconeri* Hook. have been examined for their crystalline components by extraction with organic solvents and fractionation along usual lines. Three crystalline substances which appear to be triterpenoid in nature were obtained from the petroleum-ether extract in very low yields. From the ether extract ursolic acid was obtained and from the alcoholic extract quercetin.

Acknowledgment

We thank Mr. E. Venkata Rao and Mr. M. Satyanarayana for the microanalysis.

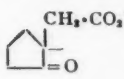
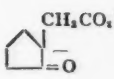
References

1. Plugge, P. C. .. *Arch. Pharm.*, 1891, **229**, 552.
2. Chopra, R. N. .. *Indigenous Drugs of India*, Art Press, Calcutta, 1933, p. 523.
3. ———, Badhwar, R. L. and Ghosh, S. *Poisonous Plants of India*, Manager of Publications, Delhi, 1949, **1**, 613.
4. Takeda, K. .. *J. Phar. Soc.*, Japan, 1941, **61**, 117.
5. Ewen, E. S. and Spring, F. S. .. *J. Chem. Soc.*, 1943, 523.
6. Jacobs, W. A. and Fleck, E. E. *J. Biol. Chem.*, 1931, **92**, 487.
7. Kuwada, S. and Matsumoto, T. *J. Phar. Soc.*, Japan, 1933, **53**, 368.
8. Heilbron, I. and Bunbury, H. M. *Dictionary of Organic Compounds*, Eyre and Spottiswoode Ltd., London, 1953, **4**, 655.
9. Josephy, E. and Radt, F. .. *Elsevier's Encyclopædia of Organic Chemistry*, Elsevier Publishing Co., Inc., New York-Amsterdam, 1940, **14**, 566.

867 57 Printed at The Bangalore Press, Bangalore City, by C. Vasudeva Rao, Superintendent,
and Published by The Indian Academy of Sciences, Bangalore.

ERRATA

(*Vol. XLVI, No.* 1, *July* 1957)

Page 81. The formula  is to be *changed* into  .

Page 87, line 10. *Read* "3-oxo*cyclo*hexane-1 : 2-dicarboxylate" *for* "2-oxo*cyclo*-hexane-1 : 2-dicarboxylate".

Page 89. Along the axis of the graphs *read* "Transmission" *for* "Absorption".

Page 89. "The infra-red spectra were taken in carbon tetrachloride solution" is to be inserted below the spectra figures.

NOTICE TO AUTHORS

Scientific papers intended for publication in the *Proceedings of the Indian Academy of Sciences* can be accepted only when they are communicated by a Fellow of the Academy whose duty shall be to satisfy himself that such communications are fit to be read at the Meeting of the Academy and published in its *Proceedings*.

Papers should not ordinarily exceed fifty pages of foolscap. MSS. should be either typewritten or written in legible hand on one side of the paper. All papers should be carefully revised by the authors and should be absolutely in final form for printing. Position for text-figures should be indicated. Each paper shall conclude with a critical summary not exceeding 350 words.

Drawings, diagrams or other illustrations should be made on larger scale (preferably) twice the size than the ones in which they are intended to appear. They should be done in Indian ink on bristol board with lettering in pencil. Scale of magnification of camera lucida tracings should be indicated by the side of drawings. In certain special cases arrangements will also be made for monochrome lithographic and other colour plates. Reduction of illustrations desired should be indicated in pencil. Appropriate legends should accompany all drawings. Names of authors are to be marked in pencil on the left-hand corner of drawing sheets. Photomicrographs should be securely mounted with colourless paste.

All tables, quotations and footnotes which will be set hereafter (beginning from Vol. I, No. 2) in types smaller than the text, should be typewritten on separate sheets and placed with the text in proper sequence. Footnotes should be numbered in Arabic numerals.

References to literature in the text should be given, whenever possible, in chronological order, only the names of authors and years of publication, in brackets, being given. They should be cited in full after the summary, the authors' names following in alphabetical order. Thus,

Name or Names of author; Name of Journal (abbreviation) with a single underline; Year of publication; Number of Volume with a double underline, and lastly page. The following would be a useful illustration:—

Bergmann and Stather . . . . . Z. Physiol. Chem., 1926, 152, 189.

Two copies of slip-proof and wherever possible, a page proof for final revision will be sent to authors. All corrections are best made on the slip-proof which should be transmitted to the Office of the Academy. All proof corrections involve heavy expenses which would be negligible if the papers are carefully revised by the authors before submission.

Fifty free reprints including plates and with cover will be supplied for each paper. Additional copies can be supplied at cost on previous intimation.

Blocks appearing in the *Proceedings* will be available for purchase by their respective authors. Orders for the same should be sent along with the corrected proofs and in any case not later than one month after the date of publication of the paper. The price charged would be 25% of the actual cost of the blocks *plus* freight and despatching charges. If the blocks are reproduced in other journals or publications, due acknowledgment should be made in them to the *Proceedings*.

The original drawings and plates of blocks appearing in the *Proceedings* will be returned to such of the authors as may require them provided the cost of despatching such originals is borne by them.

CONTENTS

PAGE

The Raman Spectrum of Calcite and Its Interpretation . . D. Krishnamurti 183

The Theory of the Anharmonic Oscillator . . . . . K. S. Viswanathan 203

Stability of Metal-Chelate Compounds of Benzopyrone Derivatives . . . . .
. . . . . G. M. Saxena and T. R. Seshadri 218

Rotational Flow of a Liquid Past a Regular Polygonal Cylinder . . . . . .
. . . . . L. V. K. Viswanadha Sarma 224

Complex Magnetic Permeability Tensor and Paramagnetic Resonance Absorption in $CuSO_4\ 5\ H_2O$ . . . . . (Miss) K. Sundaramma 232

Selective Demethylation of the 5-Methoxyl Group in Flavanones and Synthesis of Dihydrowogonin . . . S. N. Aiyar, Ishwar Dass and T. R. Seshadri 238

Crystalline Chemical Components of the Leaves of *Rhododendron falconeri* Hook. . . . . S. Rangaswami and K. Sambamurthy 245